



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification <sup>6</sup> :<br><b>A61K 7/13, 7/06</b>   | <b>A1</b> | (11) International Publication Number: <b>WO 99/13844</b><br>(43) International Publication Date: <b>25 March 1999 (25.03.99)</b>   |
| <p>(21) International Application Number: <b>PCT/US97/16406</b></p> <p>(22) International Filing Date: <b>17 September 1997 (17.09.97)</b></p> <p>(71) Applicant (for all designated States except US): <b>THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</b></p> <p>(72) Inventors; and<br/>(75) Inventors/Applicants (for US only): <b>TIAN, Minmin [CN/JP]; #203, 4-2-41, Uozaki-nishimachi, Higashinada-ku, Kobe 658 (JP). LUO, Xiaochun [CN/JP]; 5-15-703, Koyo-cho Naka, Higashinada-ku, Kobe 658 (JP). ONO, Ikuko [JP/JP]; 3-9-4-102, Sumiyoshi-honmachi, Higashinada-ku, Kobe 658 (JP).</b></p> <p>(74) Agents: <b>REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</b></p>  |           | <p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b><br/><i>With international search report.</i></p> |
| <p>(54) Title: <b>HAIR CARE COMPOSITIONS COMPRISING OPTICAL BRIGHTENERS WHICH PROVIDE UV PROTECTION</b></p> <p>(57) Abstract</p> <p>Disclosed are hair care compositions comprising: (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1nm to about 420nm; and (b) a hair care active selected from the group consisting of a detergent surfactant, a conditioning agent, a fixative polymer, and mixtures thereof. Further disclosed are hair care compositions comprising: (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1nm to about 420nm; (b) a scattering particle having an average particle size of at least about 0.03 <math>\mu</math>m; and (c) a carrier. Still further disclosed are methods of protecting the hair from UV light by applying an optical brightener to the hair.</p> |           |   |

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## HAIR CARE COMPOSITIONS COMPRISING OPTICAL BRIGHTENERS WHICH PROVIDE UV PROTECTION

5

### 10 TECHNICAL FIELD

The present invention relates to a hair care composition comprising optical brighteners which provide UV protection. The present invention further relates to a hair care composition comprising optical brighteners and scattering particles.

### 15 BACKGROUND

Ultraviolet (UV) light radiation is known to be a factor which damages the hair. Incorporation of sunscreen agents to hair care compositions have been suggested in the art. Generally, sunscreens for application to the hair require substantivity to the hair, and compatibility in hair care formulations which are often water-based. Many sunscreen agents, however, do not fully meet these requirements. Thus, the level of sunscreen agents that could be included in hair care compositions and/or the level of sunscreen agents that could deposit on the hair were limited. Consequently, hair care compositions including conventional sunscreen agents could provide only moderate UV protection.

25 Hair damage by UV light is perceived by the consumer as unfavorable appearances and less manageability of the hair. Such unfavorable appearances include alteration and fading of original color, less shine, and less luster.

A common way for alleviating the unfavorable appearances of damaged hair is to dye the hair to the color desired. Dyeing the hair would provide the consumer with a stable color of hair for a relatively long period. However, dyeing the hair is generally time-consuming, cumbersome, and messy. Thus, hair dye products are not suitable for daily use. Dyestuff may also be chemically harsh to the hair, scalp, and skin. Thus, the hair can be further damaged by dyeing.

35 Use of optical brighteners, or compounds otherwise described by names such as fluorescent whitening agents, fluorescent brighteners, or fluorescent dyes, in the hair care field has been known in the art, such as in United States

Patent 3,658,985, United States Patent 4,312,855, Canadian Patent 1,255,603, United States Patent 3,577,528, Great Britain Patent Specification 1,328,108, South African Application 676,049, European Publication 87,060, and Great Britain Patent Specification 2,307,639. Optical brighteners are a class of material which absorb UV light and re-emit the energy in the form of visible light, wherein the ultraviolet absorption is relatively strong in a broad spectrum.

Based on the foregoing, there is a need for a hair care composition which can effectively protect the hair from UV light and which can be used daily while alleviating the unfavorable appearance of the hair.

None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY

The present invention is directed to a hair care composition comprising:  
(a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000; and (b) a hair care active selected from the group consisting of a deterative surfactant, a conditioning agent, a fixative polymer, and mixtures thereof.

The present invention is further directed to a hair care composition comprising: (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000; (b) a scattering particle having an average particle size of at least about 0.03 $\mu$ m; and (c) a carrier.

The present invention is still further directed to a method of protecting the hair from UV light by applying an optical brightener to the hair.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other

materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

#### OPTICAL BRIGHTENERS

Optical brighteners are compounds which absorb ultraviolet light and re-emit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

The selected optical brighteners useful herein have a molar extinct coefficient of at least about 28,000, preferably at least about 50,000 of an absorption peak between a wavelength between about 1nm and about 420nm. Optical brighteners having such molar extinct coefficient provides effective UV protection to the hair, even when included at relatively low levels. Further, the selected optical brighteners useful herein have a strong absorption in a wide range of UV spectra, thereby provide effective UV protection in both the far-UV and near-UV regions.

The molar extinct coefficient of the optical brighteners useful herein can be measured by any UV spectrophotometer known in the art. For example, the molar extinct coefficient is measured by two UV-visible spectrophotometers, Shimadzu UV-160 and UV-2200, respectively, with the wavelength from 200nm to 600nm using a quartz cell with 1cm optical path length containing a solution of

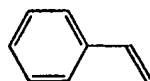
the optical brightener at an appropriate concentration. The molar extinct coefficients are derived from the peak positions.

Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. The optical brighteners useful in the present invention can be classified according to their base structures, as described hereafter. Preferable optical brighteners herein include polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles.

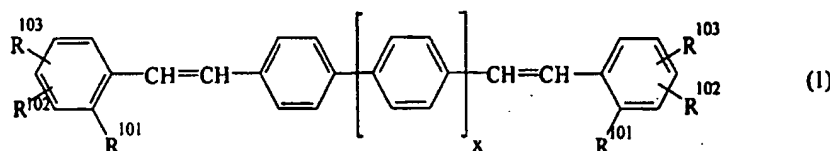
Preferably, the selected optical brighteners of the present invention are included at a level of from about 0.001% to about 20%, more preferably from about 0.01% to about 10% of the hair care composition.

#### Polystyrylstilbenes

Polystyrylstilbenes are a class of compounds having two or more of the following base structure:

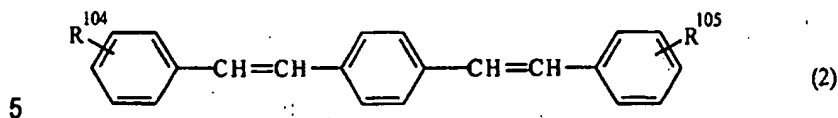


Polystyrylstilbenes useful in the present invention include those having formulae (1), (2) and (3):

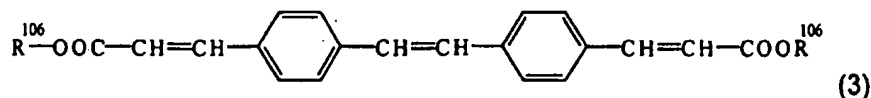


wherein  $R^{101}$  is H, OH,  $SO_3M$ , COOM,  $OSO_3M$ ,  $OPO(OH)OM$ , wherein M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- $C_1$ - $C_{30}$ -alkylammonium, mono-, di- or tri- $C_1$ - $C_{30}$ -hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of  $C_1$ - $C_{30}$ -alkyl and  $C_1$ - $C_{30}$ -hydroxyalkyl groups; or  $SO_2N(C_1-C_{30}-alkyl)_2$ ,  $O-(C_1-C_{30}-alkyl)$ , CN, Cl,  $COO(C_1-C_{30}-alkyl)$ ,  $CON(C_1-C_{30}-alkyl)_2$  or  $O(CH_2)_3N^+(CH_3)_2X^-$  wherein  $X^-$  is an anion of a chloride, bromide, iodide, formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion; CN, or alkyl of 1 to 30 carbons,  $R^{102}$  and  $R^{103}$ , independently, are H,  $SO_3M$  wherein M is as previously defined; and x is 0 or 1; wherein the compound has a

trans-coplanar orientation or cis-coplanar orientation; preferably x is 1, R<sup>101</sup> is SO<sub>3</sub>Na and R<sup>102</sup> and R<sup>103</sup> are H; wherein the compound has a trans-coplanar orientation;



wherein R<sup>104</sup> and R<sup>105</sup>, independently, are CN, COO(C<sub>1</sub>-C<sub>30</sub>-alkyl), CONHC<sub>1</sub>-C<sub>4</sub>-alkyl, or CON(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>104</sup> and R<sup>105</sup> is 2-cyano,  
10 wherein the compound has a trans-coplanar orientation; and



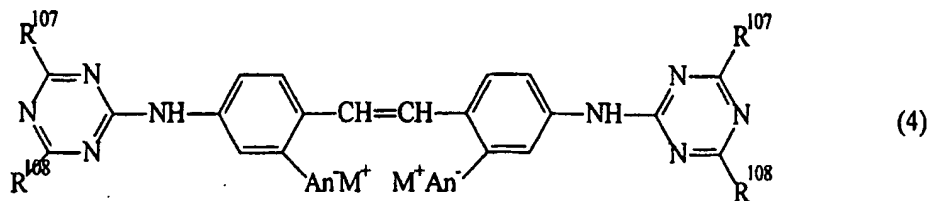
wherein each R<sup>106</sup>, independently, is H, or alkyl of 1 to 30 carbons; and wherein  
15 the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

Suitable polystyrylstilbenes include disodium-1, 4'-bis(2-sulfostyryl) bisphenyl (C.I. Fluorescent Brightener 351) with tradename Tinopal CBS-X available from Ciba Specialty Chemicals, 1,4-bis(2-cyanostyryl)benzene (C.I. Fluorescent Brightener 199) with tradename Ultraphor RN available from BASF.  
20

#### Triazinstilbenes

Triazinstilbenes are a class of compounds having both triazin and stilbene structures in the same molecule.

Triazinstilbenes useful in the present invention include those having  
25 formulae (4):

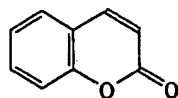


- wherein R<sup>107</sup> and R<sup>108</sup>, independently, are phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, N(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH), NH<sub>2</sub>, N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>, OCH<sub>3</sub>, Cl, NH-(CH<sub>2</sub>)<sub>1-4</sub>SO<sub>3</sub>H or NH-(CH<sub>2</sub>)<sub>1-4</sub>OH; An<sup>-</sup> is an anion of a carboxylate, sulfate, sulfonate, or phosphate, and M is as previously defined,
- 5 wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>107</sup> is 2, 5-disulfophenylamino and each R<sup>108</sup> is morpholino; or each R<sup>107</sup> is 2, 5-disulfophenylamino and each R<sup>108</sup> is N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; or each R<sup>107</sup> is 3-sulfophenyl and each R<sup>108</sup> is NH(CH<sub>2</sub>CH<sub>2</sub>OH) or N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>; or each R<sup>107</sup> is 4-sulfophenyl and each R<sup>108</sup> is
- 10 N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>; and in each case, the sulfo group is SO<sub>3</sub>M in which M is sodium; wherein the compound has a trans-coplanar orientation.

- Suitable triazinstilbenes include 4,4'-bis-[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-morpholine-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate
- 15 with tradename Tinopal AMS-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-(2-hydroxyethyl)methyl amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal 5BM-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate,
- 20 4,4'-bis-[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, and 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid.

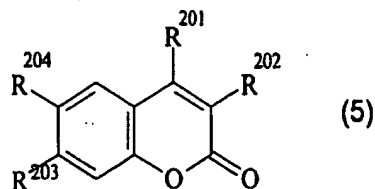
#### Hydroxycoumarins

- 25 Hydroxycoumarins are a class of compounds having the following base coumarin structure and having at least one hydroxy moiety:

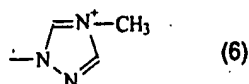


- 30 Hydroxycoumarins useful in the present invention include those having formulae (5):

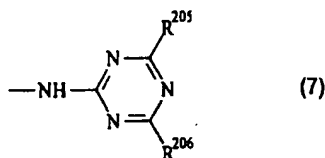




wherein R<sup>201</sup> is H, OH, Cl, CH<sub>3</sub>, CH<sub>2</sub>COOH, CH<sub>2</sub>SO<sub>3</sub>H, CH<sub>2</sub>OSO<sub>3</sub>H, or CH<sub>2</sub>OPO(OH)OH, R<sup>202</sup> is H, phenyl, COO-C<sub>1</sub>-C<sub>30</sub>-alkyl, glucose, or a group of  
 5 formula (6):



and R<sup>203</sup> is OH, or O-C<sub>1</sub>-C<sub>30</sub>-alkyl, and R<sup>204</sup> is OH or O-C<sub>1</sub>-C<sub>30</sub> alkyl,  
 10 glycoside, or a group of the following formula (7):



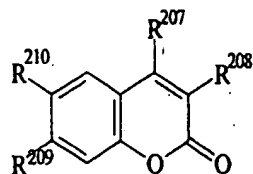
wherein R<sup>205</sup> and R<sup>206</sup> are independently, phenylamino, mono- or disulfonated  
 15 phenylamino, morpholino, N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, N(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH), NH<sub>2</sub>, N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, OCH<sub>3</sub>, Cl, NH-(CH<sub>2</sub>)<sub>1-4</sub>SO<sub>3</sub>H or NH-(CH<sub>2</sub>)<sub>1-4</sub>OH.

Suitable hydroxycoumarins include 6,7-dihydroxycoumarin available from Wako Chemicals, 4-methyl-7-hydroxycoumarin available from Wako Chemicals, 4-methyl-6,7-dihydroxycoumarin available from Wako Chemicals, esculin  
 20 available from Wako Chemicals, and umbelliferone (4-hydroxycoumarin) available from Wako Chemicals.

#### Aminocoumarins

Aminocoumarins are a class of compounds having the base coumarin structure and having at least one amino moiety.

25 Aminocoumarins useful in the present inventions include those having formulae (8):



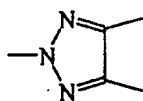
(8)

- wherein  $R^{207}$  is H, Cl,  $CH_3$ ,  $CH_2COOH$ ,  $CH_2SO_3H$ ,  $CH_2OSO_3H$ , or  $CH_2OPO(OH)OH$ ,  $R^{208}$  is H, phenyl, or  $COOC_1-C_{30}$  alkyl, and  $R^{209}$  and  $R^{210}$  are independently H,  $NH_2$ ,  $N(C_1-C_{30}alkyl)_2$ ,  $NHC_1-C_{30}alkyl$ , or  $NHCOC_1-C_{30}alkyl$ .

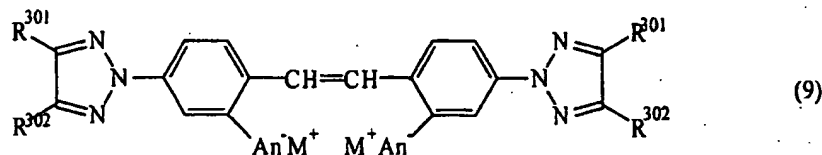
Suitable aminocoumarins include 4-methyl-7,7'-diethylamino coumarin with tradename Calcofluor-RWP available from BASF, 4-methyl-7,7'-dimethylamino coumarin with tradename Calcofluor-LD available from BASF.

#### 10 Triazoles

Triazoles are a class of compounds having the following base structure:

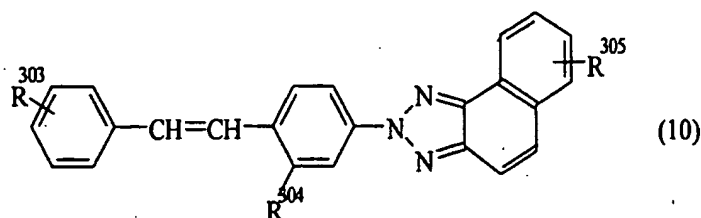


- 15 Triazoles useful in the present inventions include those having formulae (9) through (12) and (15) through (20):

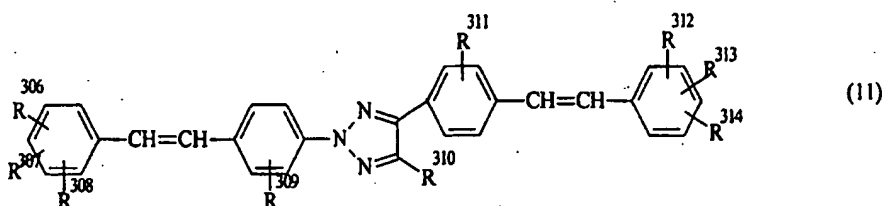


(9)

- 20 wherein  $R^{301}$  and  $R^{302}$ , independently, are H,  $C_1-C_{30}alkyl$ , phenyl or monosulfonated phenyl;  $An^-$  and  $M^+$  are as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably  $R^{301}$  is phenyl,  $R^{302}$  is H and  $M$  is sodium; wherein the compound has a trans-coplanar orientation;



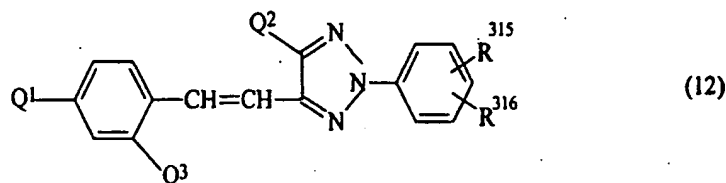
- wherein R<sup>303</sup> is H or Cl; R<sup>304</sup> is SO<sub>3</sub>M, SO<sub>2</sub>N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, SO<sub>2</sub>O-phenyl or CN; R<sup>305</sup> is H, SO<sub>3</sub>M, COOM, OSO<sub>3</sub>M, or OPO(OH)OM; and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>303</sup> and R<sup>305</sup> are H and R<sup>304</sup> is SO<sub>3</sub>M in which M is Na; wherein the compound has a trans-coplanar orientation;



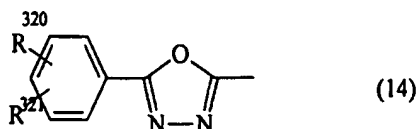
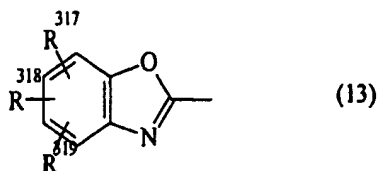
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- wherein each of R<sup>306</sup> and R<sup>312</sup> independently represents H, a sulfonic acid group or the salts, esters or amides thereof; a carboxylic acid group or the salts, esters or amides thereof; a cyano group, a halogen atom, an unsubstituted or substituted alkylsulfonyl, arylsulfonyl, alkyl, alkoxy, aralkyl, aryl, aryloxy, aralkoxy or cycloalkyl radical, an unsubstituted or substituted 5-membered heterocyclic ring containing 2 to 3 nitrogen atoms or one oxygen atom and 1 or 2 nitrogen atoms, or together with R<sup>307</sup> and R<sup>313</sup> they represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R<sup>307</sup> and R<sup>313</sup> independently represents H, a sulfonic acid group or the salts, esters or amides thereof; a carboxylic acid group or the salts, esters or amides thereof; a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with R<sup>306</sup> and R<sup>312</sup> represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R<sup>308</sup> and R<sup>314</sup> independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of R<sup>309</sup> and R<sup>311</sup> independently represents H, a halogen atom, a cyano group a sulonic acid group or the salts, esters or amides thereof, or a carboxylic acid group or the

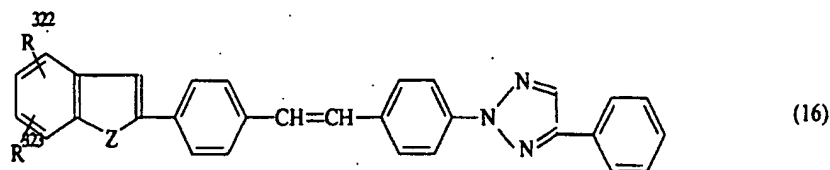
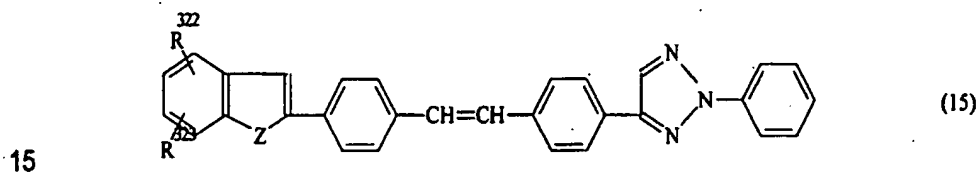
salts, esters or amides thereof, and R<sup>310</sup> independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, sulfonic acid groups, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;



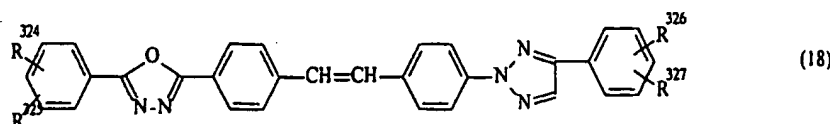
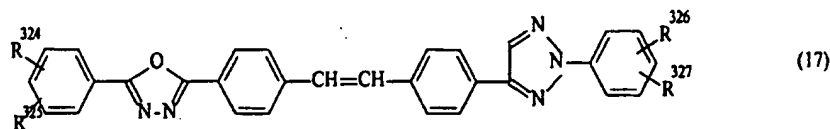
wherein Q<sup>1</sup> denotes one of the ring systems (13) or (14);

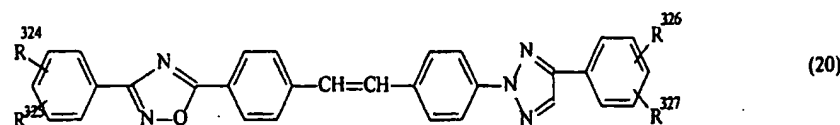
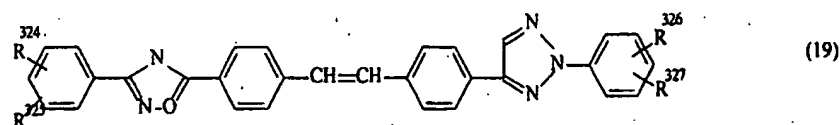


- and wherein R<sup>317</sup> denotes H, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with C<sub>1</sub>-C<sub>30</sub> carbon atoms in the alkyl part, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R<sup>318</sup>, denotes alkylene with 3 to 30 carbon atoms, R<sup>318</sup> denotes H or alkyl with 1 to 30 carbon atoms or, conjointly with R<sup>317</sup>, denotes alkylene with 3 to 30 carbon atoms, R<sup>319</sup> denotes H or methyl, R<sup>320</sup> denotes H, alkyl with 1 to 30 carbon atoms, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R<sup>321</sup>, denotes a fused benzene ring, R<sup>321</sup> denotes H or Cl or conjointly with R<sup>320</sup>, denotes a fused benzene ring, R<sup>315</sup> denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms or Cl, R<sup>316</sup> denotes H or Cl, Q<sup>2</sup> denotes H, Cl alkyl with 1 to 30 carbon atoms or phenyl and Q<sup>3</sup> denotes H or Cl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;



- wherein R<sup>322</sup> denotes H, Cl, methyl, phenyl, benzyl, cyclohexyl or methoxy, R<sup>323</sup> denotes H or methyl and Z denotes O or S; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation; and
- 20



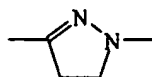


wherein R<sup>324</sup> denotes H, Cl, alkyl with 1 to 30 carbon atoms, phenylalkyl with 1 to 30 carbon atoms, phenyl or alkoxy with 1 to 30 carbon atoms, or R<sup>324</sup> jointly with R<sup>325</sup> denotes a fused benzene radical, R<sup>325</sup> denotes H or methyl or R<sup>325</sup> jointly with R<sup>324</sup> denotes a fused benzene radical, R<sup>326</sup> denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms or alkylsulfonyl with 1 to 30 carbon atoms and R<sup>327</sup> denotes H, Cl, methyl or methoxy; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

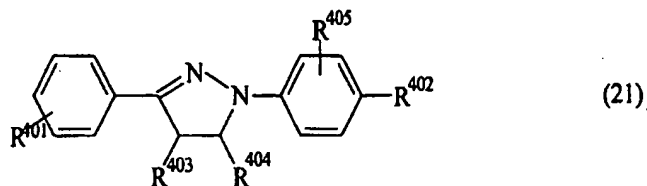
Suitable triazoles include 2-(4-styryl-3-sulfophenyl)-2H-naphtho[1,2-d]triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

#### 15 Pyrazolines

Pyrazolines are a class of compounds having the following base structure:



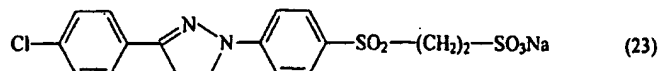
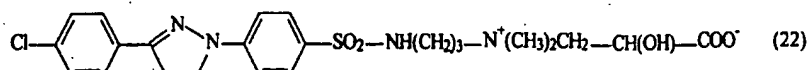
20 Pyrazolines useful in the present invention include those having formulae (21) through (23):



25 wherein R<sup>401</sup> is H, Cl or N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, R<sup>402</sup> is H, Cl, SO<sub>3</sub>M, SO<sub>2</sub>NH<sub>2</sub>, SO<sub>2</sub>NH-(C<sub>1</sub>-C<sub>30</sub>-alkyl), COO-C<sub>1</sub>-C<sub>30</sub>-alkyl, SO<sub>2</sub>-C<sub>1</sub>-C<sub>30</sub>-alkyl, SO<sub>2</sub>NH(CH<sub>2</sub>)<sub>1-4</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> or SO<sub>2</sub>(CH<sub>2</sub>)<sub>1-4</sub>N<sup>+</sup>H(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>An<sup>-</sup>, R<sup>403</sup> and R<sup>404</sup> are the

same or different and each is H, C<sub>1</sub>-C<sub>30</sub>alkyl or phenyl and R<sup>405</sup> is H or Cl; and An<sup>-</sup> and M are as previously defined, preferably R<sup>401</sup> is Cl, R<sup>402</sup> is SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>An<sup>-</sup> in which An<sup>-</sup> is phosphite and R<sup>403</sup>, R<sup>404</sup> and R<sup>405</sup> are each H; and formulae (22) and (23) shown below.

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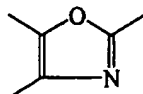
Suitable pyrazolines include 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline (C.I. Fluorescent Brightener 121) with tradename Blankophor DCB available from Bayer, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-pyrazoline, 1-<4-[N-[3-(N,N,N-trimethylammonio)propyl]-amidosulfonyl]phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate, and 1-<4-[2-[1-methyl-2-(N,N-dimethylamino)ethoxy]ethylsulfonyl]phenyl>-3-(4-chlorophenyl)-2-pyrazoline methylsulfate.

15

#### Oxazoles

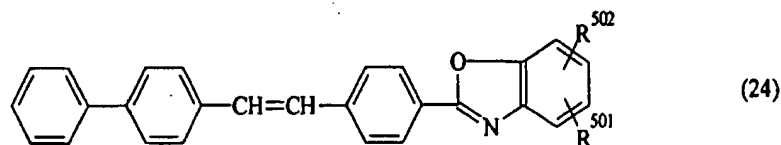
Oxazoles are a class of compounds having the following base structure:

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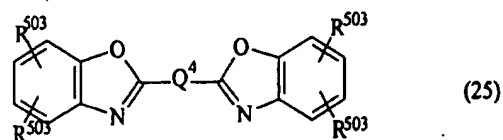
Oxazoles useful in the present inventions include those having formulae (24), (25), (26) and (27):

25



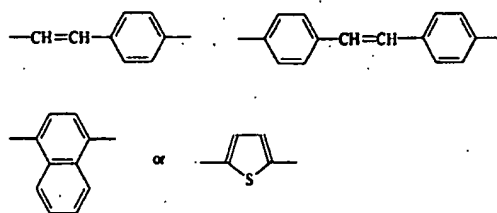
wherein R<sup>501</sup> and R<sup>502</sup>, independently, are H, Cl, C<sub>1</sub>-C<sub>30</sub>alkyl or SO<sub>2</sub>-C<sub>1</sub>-C<sub>30</sub>alkyl, wherein the compound has a trans-coplanar orientation or cis-coplanar

orientation; preferably  $R^{501}$  is 4- $\text{CH}_3$  and  $R^{502}$  is 2- $\text{CH}_3$  wherein the compound has a trans-coplanar orientation;



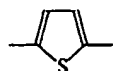
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wherein  $R^{503}$ , independently, is H,  $\text{C}(\text{CH}_3)_3$ ,  $\text{C}(\text{CH}_3)_2$ -phenyl,  $\text{C}_1$ - $\text{C}_{30}$ alkyl or  $\text{COO-C}_1$ - $\text{C}_{30}$ alkyl, preferably H and  $Q^4$  is  $-\text{CH}=\text{CH}-$ ;



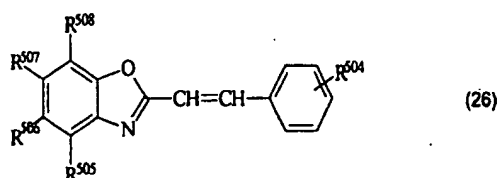
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preferably



or one group  $R^{503}$  in each ring is 2-methyl and the other  $R^{503}$  is H and  $Q^4$  is  $-\text{CH}=\text{CH}-$ ; or one group  $R^{503}$  in each ring is 2- $\text{C}(\text{CH}_3)_3$  and the other  $R^{503}$  is H; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;

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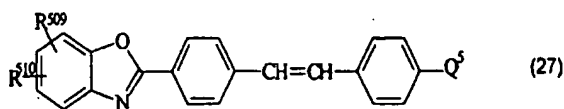


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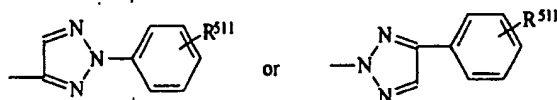
wherein  $R^{504}$  is CN, Cl,  $\text{COO-C}_1$ - $\text{C}_{30}$ alkyl or phenyl;  $R^{505}$  and  $R^{506}$  are the atoms required to form a fused benzene ring or  $R^{506}$  and  $R^{508}$ , independently, are H or  $\text{C}_1$ - $\text{C}_{30}$ alkyl; and  $R^{507}$  is H,  $\text{C}_1$ - $\text{C}_{30}$ alkyl or phenyl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably  $R^{504}$  is a 4-phenyl group and each of  $R^{505}$  to  $R^{508}$  is H; wherein the compound has a trans-coplanar orientation; and

25





- wherein R<sup>509</sup> denotes H, Cl, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with 1 to 3 carbon atoms in the alkyl part, phenyl or alkoxy with 1 to 30 carbon atoms, R<sup>510</sup> denotes H or alkyl with 1 to 30 carbon atoms, and Q<sup>5</sup> denotes a radical;

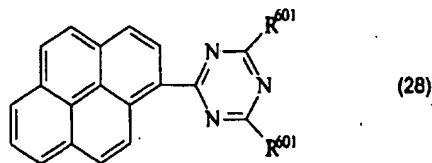


- wherein R<sup>511</sup> represents H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms, unsubstituted sulfamoyl or sulfamoyl which is monosubstituted or disubstituted by alkyl or hydroxyalkyl with 1 to 30 carbon atoms or represents alkylsulfonyl with 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

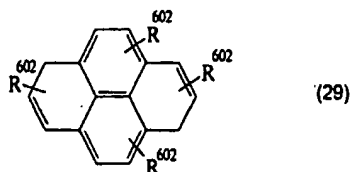
Suitable oxazoles include 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, and 2-(4-methoxycarbonylstyryl)benzoxazole.

#### Pyrenes

- Pyrenes useful in the present invention include those having formulae (28) and (29):



wherein each R<sup>601</sup>, independently, is C<sub>1</sub>-C<sub>30</sub>alkoxy; preferably methoxy; and

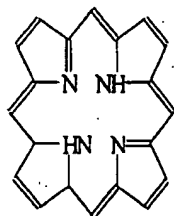


wherein each R<sup>602</sup>, independently, is H, OH, or SO<sub>3</sub>M, wherein M is as previously defined, sulfonated phenylamino, or anilino.

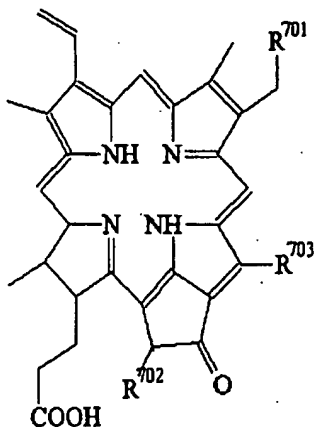
Suitable pyrenes include 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine (C.I. Fluorescent Brightener 179) with tradename Fluolite XMF, 8-hydroxy-1,3,6-pyrenetrisulfonic acid (D&C Green No.8), and 3-hydroxy-5,8,10-trisulphanilic pyrene.

#### Porphyrins

Porphyrins useful in the present invention include those having formulae (30), (31), and (32):

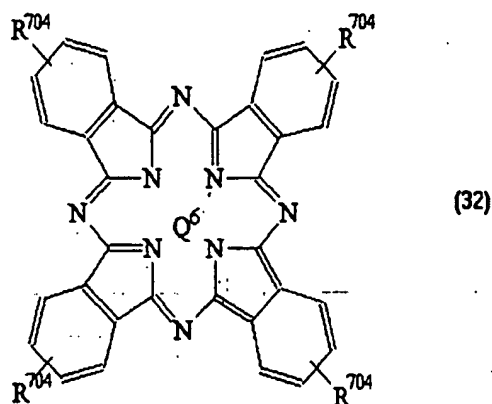


(30)



(31)

wherein R<sup>701</sup> is CH<sub>3</sub> or CHO, R<sup>702</sup> is H or COOC<sub>1</sub>-C<sub>30</sub> alkyl, and R<sup>703</sup> is H or an alkyl group having 1 to 30 carbons; and

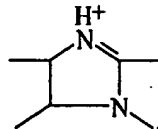


wherein each  $R^{704}$ , independently, is H,  $SO_3M$ ,  $COOM$ ,  $OSO_3M$ , or  $OPO(OH)OM$ , wherein M is as previously defined, halide, or alkyl of 1 to 30 carbons; and  $Q^6$  is Cu, Mg, Fe, Cr, Co, or mixtures thereof with cationic charges.

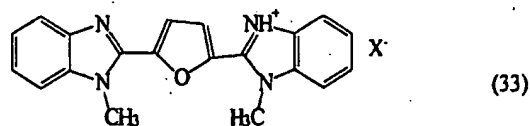
Suitable porphyrins include porphyrin available from Wako Chemicals and Copper II phthalocyanine available from Wako Chemicals.

#### Imidazoles

Imidazoles are a class of compounds having the following base structure:



Imidazoles useful in the present invention include those having formulae (33):



wherein  $X^-$  is as previously defined.

Suitable imidazoles include those with tradename of C.I. Fluorescence Brightener 352, or Uvtext AT available from Ciba Speciality Chemical.

The hair care compositions of the present invention herein including optical brighteners provide benefits to the hair in three areas. First, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet

light, as described in detail above. Second, optical brighteners herein alter the color of the hair by emitting light in the visible range. Third, optical brighteners herein enhance the shine of the hair by emitting light in the visible range.

#### HAIR CARE ACTIVE

5       The hair care compositions of the present invention comprise a component which characterizes the form and function of the product. Product forms useful herein include, but are not limited to, shampoo, conditioner, treatment, mousse, spray, lotion, gel, and cream products, all of which can be designed for rinse-off or leave-on convenience. Product functions useful herein  
10       include, but are not limited to, cleaning, conditioning, and styling products. To make these products, a hair care active selected from the group consisting of a deterative surfactant, a conditioning agent, a fixative polymer, and mixtures thereof are comprised. The hair care actives and their levels are selected by one skilled in the art depending on the desired characteristic of the product.

#### 15       DETERATIVE SURFACTANT

Compositions herein may include a deterative surfactant. The deterative surfactants herein are those suitable for cleansing the hair. Deterative surfactants useful herein include anionic surfactants, amphoteric and zwitterionic surfactants, and nonionic surfactants.

20       The deterative surfactants, when present, are preferably included at a level of from about 0.01% to about 75% by weight of the composition. Two or more surfactants can be used.

#### Anionic Surfactant

Anionic surfactants useful herein include alkyl and alkyl ether sulfates.  
25       These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as ammonium, alkanolammonium (e.g., triethanolammonium), a monovalent metal cation (e.g., sodium and potassium), or a polyvalent metal cation (e.g.,  
30       magnesium and calcium). Preferably, M should be chosen such that the anionic surfactant component is water soluble. The anionic surfactant or surfactants should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the anionic surfactant be soluble in the composition hereof.

35       Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration,

and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, 5 Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, New York, USA), 1988 (ISBN 0-89573-399-0), which is incorporated by reference herein in its entirety.

In the alkyl and alkyl ether sulfates described above, preferably R has from about 8 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. 10 The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm oil, tallow, or the like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are 15 reacted with 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

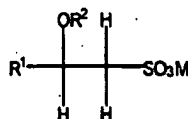
Specific examples of alkyl ether sulfates which can be used are sodium 20 and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 8 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 25 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% by weight C<sub>12-13</sub> compounds; from about 60% to about 100% by weight of C<sub>14-15-16</sub> compounds, from 0% to about 20% by weight of C<sub>17-18-19</sub> compounds; from about 3% to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of 30 compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Other suitable anionic surfactants are the water-soluble salts of organic, 35 sulfuric acid reaction products of the general formula [R<sup>1</sup>-SO<sub>3</sub>-M] where R<sup>1</sup> is selected from the group consisting of a straight or branched chain, saturated

aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 8 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 8 to about 18 carbon atoms and a sulfonating agent, e.g., SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C<sub>8-18</sub> n-paraffins.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278, which are incorporated by reference herein in their entirety.

Another class of anionic surfactants suitable for use in the shampoo compositions are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:

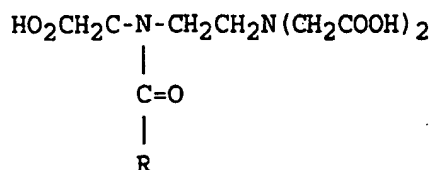


where R<sup>1</sup> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sup>2</sup> is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference in their entirety. Preferred anionic surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, ammonium cocoyl sulfate,

ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, and sodium dodecyl benzene sulfonate, and mixtures thereof.

Other anionic surfactants for use herein include polyhydrophilic anionic surfactants. By "polyhydrophilic" herein, is meant a surfactant that has at least two hydrophilic groups which provide a hydrophilic nature. Polyhydrophilic surfactants useful herein are only those having at least two hydrophilic groups in the molecule, and is not intended to encompass those which only have one hydrophilic group. One molecule of the polyhydrophilic anionic surfactant herein may comprise the same hydrophilic groups, or different hydrophilic groups. Specifically, the polyhydrophilic anionic surfactants comprise at least one group selected from the group consisting of carboxy, hydroxy, sulfate, sulfonate, and phosphate. Suitable polyhydrophilic anionic surfactants are those which comprise at least one of a carboxy, sulfate, or sulfonate group, more preferably those which comprise at least one carboxy group.

Nonlimiting examples of polyhydrophilic anionic surfactants include N-acyl-L-glutamates such as N-cocoyl-L-glutamate and, N-lauroyl-L-glutamate, laurimino dipropionate, N-acyl-L-aspartate, di-(N-lauroyl N-methyl taurate), polyoxyethylene laurylsulfosuccinate, disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetra sodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; the diamyl ester of sodium sulfosuccinic acid; the dihexyl ester of sodium sulfosuccinic acid; and the dioctyl ester of sodium sulfosuccinic acid, and 2-cocoalkyl N-carboxyethyl N-carboxyethoxyethyl imidazolinium betaine, lauroamphohydroxypropylsulfonate, cocoglyceryl ether salts, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and those of the following formula:



5

wherein R is an alkyl of 8 to 18 carbons. Other polyhydrophilic anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms.

10 The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or

15 gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO<sub>2</sub>, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO<sub>2</sub>, etc., when used in the gaseous form. The α-olefins from which the olefin sulfonates are derived are mono-olefins having about 8 to about 24 carbon atoms, preferably about 10 to about 16 carbon atoms.

20 Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A specific α-olefin sulfonate mixture of the above type is

25 described more fully in U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967, which is incorporated by reference herein in its entirety.

Another class of polyhydrophilic anionic surfactants are amino acid surfactants which are surfactants that have the basic chemical structure of an

30 amino acid compound, i.e., that contains a structural component of one of the naturally-occurring amino acids. It is understood by the artisan that some surfactants may be regarded as both a polyhydrophilic anionic surfactant, and an amino acid surfactant. These surfactants are suitable anionic surfactants.

Nonlimiting examples of amino acid surfactants include, N-

35 cocoylalaninate, N-acyl-N-methyl-β-alanate, N-acylsarcosinate; N-alkylamino propionates and N-alkyliminodipropionates, specific examples of which include N-lauryl-β-amino propionic acid or salts thereof, and N-lauryl-β-imino-dipropionate, N-acyl-DL-alaninate, sodium lauryl sarcosinate, sodium lauroyl



sarcosinate, lauryl sarcosine, cocoyl sarcosine, N-acyl-N-methyl taurate, lauroyl taurate, and lauroyl lactylate.

Commercially available anionic surfactants suitable are N-acyl-L-glutamate with a tradename AMISOFT CT-12S, N-acyl potassiumglycine with a tradename AMILITE GCK-12, lauroyl glutamate with a tradename AMISOFT LS-11, and N-acyl-DL-alaninate with tradename AMILITE ACT12 supplied by Ajinomoto; acylaspartate with tradenames ASPARACK and AAS supplied by Mitsubishi Chemical; and acyl derivatives of tradename ED3A supplied by Hampshire Chemical Corp.

Optionally the counter ion of anionic surfactants may be polyvalent cations. It has been found that these anionic surfactants, along with the cationic conditioning agents, and polyvalent metal cations as described later, form a coacervate in the compositions. Cationic conditioning agents may be included in the present composition to provide a shampoo which both cleanse and condition the hair from a single product.

Coacervate formulation is dependent upon a variety of criteria such as molecular weight, component concentration, and ratio of interacting ionic components ionic strength, charge density of the cationic and anionic components, pH, and temperature. Coacervate systems and the effect of these parameters are known in the art.

It is believed to be particularly advantageous, for the anionic surfactants and the polyvalent metal cations at certain levels to be present with the cationic conditioning agents in a coacervate phase. The coacervates formed in the compositions are believed to readily deposit on the hair upon diluting the coacervate with abundant water, i.e., rinsing of the shampoo.

Without being bound by theory, it is believed that the coacervates provide two major effects to the present shampoo composition. First, it reduces the Critical Micelle Concentration (hereinafter "CMC") of the composition. The reduction of the CMC relates to reduction of the surface tension, thereby improving lather performance. Second, the existence of the anionic surfactants along with the polyvalent metal cations expand the coacervate region in the composition. As the cationic conditioning agents in the composition are mainly delivered to the hair via these coacervates, expansion of the coacervate region results in delivery of more cationic conditioning agents to the hair. Consequently, compositions which both cleanse and condition the hair from a single product,

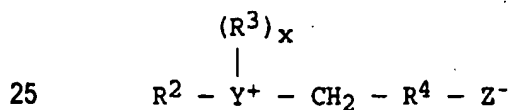
which have improved overall conditioning benefits and improved lathering are provided.

Techniques of analysis of formation of complex coacervates are known in the art. For example, microscopic analysis of the shampoo compositions, at any  
 5 chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the shampoo composition.

#### 10 Amphoteric And Zwitterionic Surfactant

Amphoteric surfactants for use herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18  
 15 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Zwitterionic surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains  
 20 an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



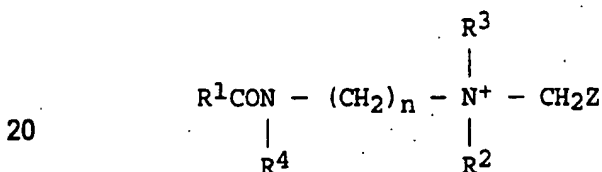
where  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group  
 30 containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

35 Examples of amphoteric and zwitterionic surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-

hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidodimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C<sub>8</sub>-C<sub>18</sub> hydrocarbylamidopropyl hydroxysultaines, especially C<sub>8</sub>-C<sub>14</sub> hydrocarbylamidopropylhydroxysultaines, e.g., laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula  $\text{RNH}(\text{CH}_2)_n\text{COOM}$ , the iminodialkanoates of the formula  $\text{RN}[(\text{CH}_2)_m\text{COOM}]_2$  and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Other suitable amphoteric surfactants include those represented by the formula :

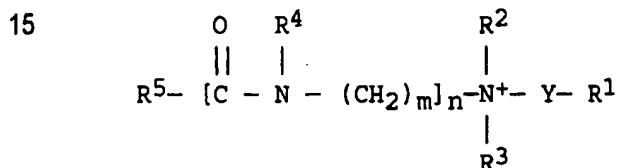


wherein R<sup>1</sup> is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, preferably C<sub>8</sub> - C<sub>16</sub>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of hydrogen, -CH<sub>2</sub>CO<sub>2</sub>M, -CH<sub>2</sub>CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, or -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>H wherein m is an integer from 1 to about 25, and R<sup>4</sup> is hydrogen, -CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R<sup>2</sup>. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkari Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants, i.e. zwitterionic surfactants, suitable for use in the conditioning compositions are those represented by the formula:



wherein: R<sup>1</sup> is a member selected from the group consisting of

COOM and CH(OH)CH<sub>2</sub>SO<sub>3</sub>M

R<sup>2</sup> is lower alkyl or hydroxyalkyl; R<sup>3</sup> is lower alkyl or hydroxyalkyl; R<sup>4</sup> is a member selected from the group consisting of hydrogen and lower alkyl; R<sup>5</sup> is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such

as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as  
5 cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl- $\alpha$ -carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) carboxymethylbetaine, oleyldimethyl- $\gamma$ -carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)- $\alpha$ -carboxyethylbetaine, etc. The sulfobetaines may be  
10 represented by cocodimethylsulfopropylbetaine, stearyldimethylsulfopropyl betaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful in the conditioning compositions include the amidocarboxybetaines, such as cocamido dimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine,  
15 cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl) carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethyl sulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

## 20 Nonionic Surfactant

The compositions of the present invention can comprise a nonionic surfactant. Nonionic surfactants include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

25 Preferred nonlimiting examples of nonionic surfactants for use in the shampoo compositions include the following:

(1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain  
30 configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

35 (3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations,

with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 8 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula [  $R^1R^2R^3N \rightarrow O$  ]

5 where  $R^1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R^2$  and  $R^3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

10 (5) long chain tertiary phosphine oxides of the formula [  $RR'R''P \rightarrow O$  ] where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

15 (6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

20 (7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which is incorporated herein by reference in its entirety, and which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a  
25 polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

30 (8) polyoxyethylene alkyl ethers such as those of the formula  $RO(CH_2CH_2)_nH$  and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula  $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ , wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

35 CONDITIONING AGENTS

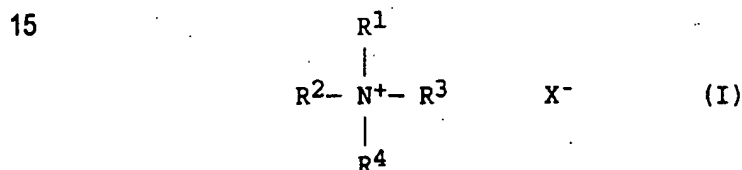
Compositions herein may include a conditioning agent. Conditioning agents useful herein are those suitable for conditioning or treating the hair. Conditioning agents useful herein include cationic surfactants, high melting point compounds, oily compounds, cationic polymers, silicone compounds, and nonionic polymers.

The conditioning agents, when present, are preferably included at a level of from about 0.01% to about 30% by weight of the composition. When two or more conditioning agents are used, preferably each conditioning agents does not exceed about 20% by weight of the composition.

#### 10 Cationic Surfactant

The cationic surfactants useful herein are any known to the artisan.

Among the cationic surfactants useful herein are those corresponding to the general formula (I):

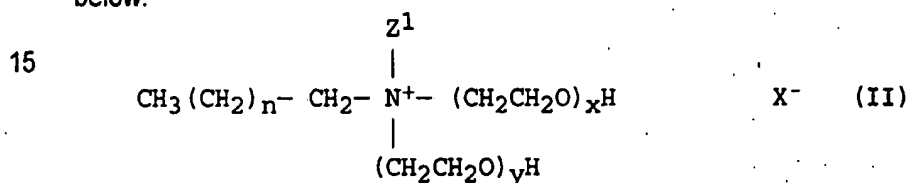


wherein at least one of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals.

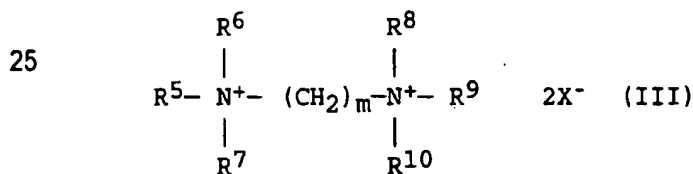
The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are independently selected from  $C_1$  to about  $C_{22}$  alkyl. Nonlimiting examples of cationic surfactants useful include the materials having the following CTFA designations: quaternium-8, quaternium-24, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-62, quaternium-70, quaternium-72, quaternium-75, quaternium-77,

quaternium-78, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

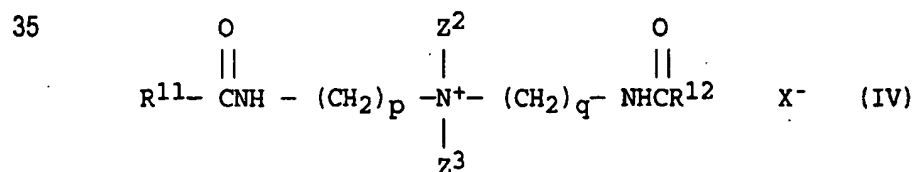
Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the  $R^1 - R^4$  radicals contain one or more hydrophilic moieties selected, from alkoxy (preferably  $C_1 - C_3$  alkoxy), polyoxyalkylene (preferably  $C_1 - C_3$  polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VII) below:



wherein  $n$  is from 8 to about 28,  $x+y$  is from 2 to about 40,  $Z^1$  is a short chain alkyl, preferably a  $C_1 - C_3$  alkyl, more preferably methyl, or  $-(CH_2CH_2O)_zH$  wherein  $x+y+z$  is up to 60, and  $X$  is a salt forming anion as defined above;



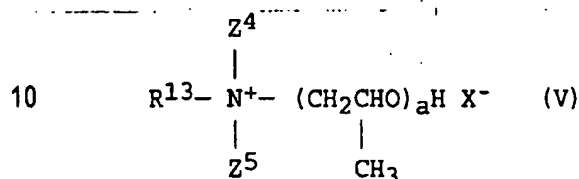
wherein  $m$  is 1 to 5, one or more of  $R^5$ ,  $R^6$ , and  $R^7$  are independently an  $C_1 - C_{30}$  alkyl, the remainder are  $-CH_2CH_2OH$ , one or two of  $R^8$ ,  $R^9$ , and  $R^{10}$  are independently an  $C_1 - C_{30}$  alkyl, and remainder are  $-CH_2CH_2OH$ , and  $X$  is a salt forming anion as mentioned above;



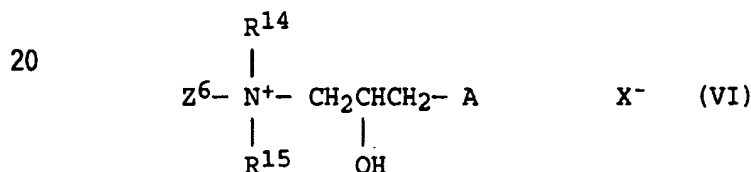
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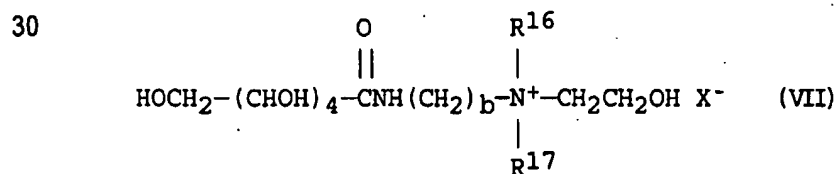
- wherein  $Z^2$  is an alkyl, preferably a  $C_1 - C_3$  alkyl, more preferably methyl, and  $Z^3$  is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl,  $p$  and  $q$  independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2,  $R^{11}$  and  $R^{12}$ , independently, are substituted or unsubstituted hydrocarbyls, preferably  $C_{12} - C_{20}$  alkyl or alkenyl, and  $X$  is a salt forming anion as defined above;



- wherein  $R^{13}$  is a hydrocarbyl, preferably a  $C_1 - C_3$  alkyl, more preferably methyl,  $Z^4$  and  $Z^5$  are, independently, short chain hydrocarbyls, preferably  $C_2 - C_4$  alkyl or alkenyl, more preferably ethyl,  $a$  is from 2 to about 40, preferably from about 7 to about 30, and  $X$  is a salt forming anion as defined above;



- wherein  $R^{14}$  and  $R^{15}$ , independently, are  $C_1 - C_3$  alkyl, preferably methyl,  $Z^6$  is a  $C_{12} - C_{22}$  hydrocarbyl, alkyl carboxy or alkylamido, and  $A$  is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and  $X$  is a salt forming anion as defined above;



- wherein  $b$  is 2 or 3,  $R^{16}$  and  $R^{17}$ , independently are  $C_1 - C_3$  hydrocarbyls preferably methyl, and  $X$  is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful include the materials having the following CTFA designations: quaternium-16, quaternium-61, quaternium-71, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79

hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein. Highly preferred compounds include commercially available materials of the following tradenames; VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, 5 MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable 10 cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amido substituted tertiary fatty amines. Such amines, useful herein, include stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldimethylamine, 15 stearamidoethyldiethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldimethylamine, palmitamidoethyldiethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldimethylamine, behenamidoethyldiethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, 20 arachidamidoethyldimethylamine, arachidamidoethyldiethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and 25 arachidylbehenylamine. These amines can also be used in combination with acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful are disclosed in U.S. 30 Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

#### High Melting Point Compound

35 The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty

alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of

compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol; i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C<sub>1</sub>-C<sub>30</sub> alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

### Oily Compound

The compositions comprise an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds  
5 useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second  
10 oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International  
Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by  
15 reference herein in their entirety.

### First Oily Compound

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols  
20 can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

25 The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic  
30 acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol  
35 derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl

oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a tradename ENUJERUBU TP3SO available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

#### Second Oily Compound

The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C<sub>2-6</sub> alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA),  $\alpha$ -olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co., and trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co.

#### Cationic Polymers

As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g.,

Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, 5 terpolymers, etc. of quaternary ammonium or cationic amine-substituted ~~monomer units and other non-cationic units~~ referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, 10 Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and 15 dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub> - C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub> - C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene 20 glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, 25 and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C<sub>1</sub> - C<sub>7</sub> alkyl, more preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, and X is an anion which forms a 30 water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, 35 trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings



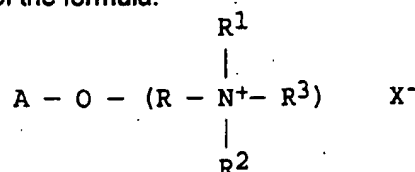
such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub> - C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls. Suitable amine-substituted vinyl monomers for use  
 5 herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl-groups are preferably C<sub>1</sub> - C<sub>7</sub> hydrocarbyls, more preferably C<sub>1</sub> - C<sub>3</sub> alkyls.

The cationic polymers hereof can comprise mixtures of monomer units  
 10 derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance  
 15 Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf  
 20 Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral  
 25 acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

30 Cationic polysaccharide polymer materials suitable for use herein include those of the formula:



35

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group  
5 containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less; and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in  
10 their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with  
15 lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

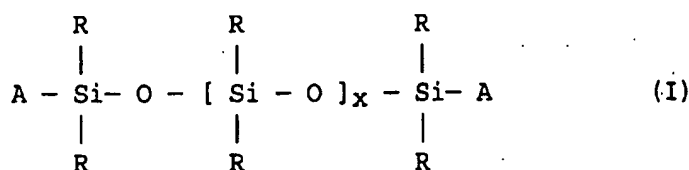
Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially  
20 available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

### Silicone Compounds

The conditioning agents useful herein include silicone compounds. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone.

Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are

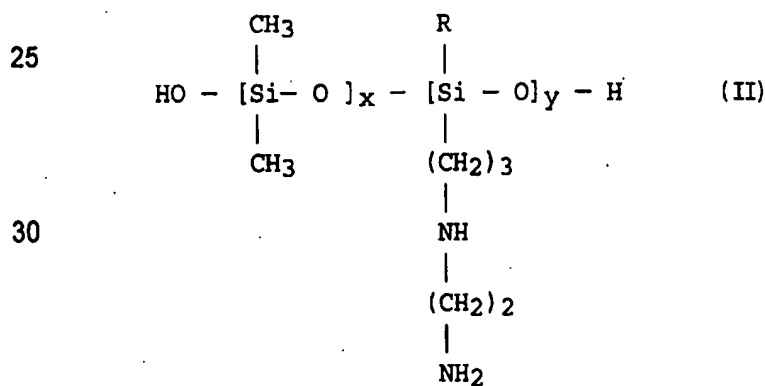
available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the  
 5 General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher.  
 10 When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

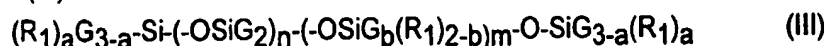
The silicone compounds that can be used include, for example, a  
 15 polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

20 Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)

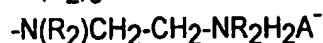
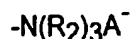
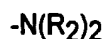
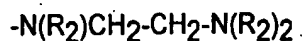


35 wherein R is CH<sub>3</sub> or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)

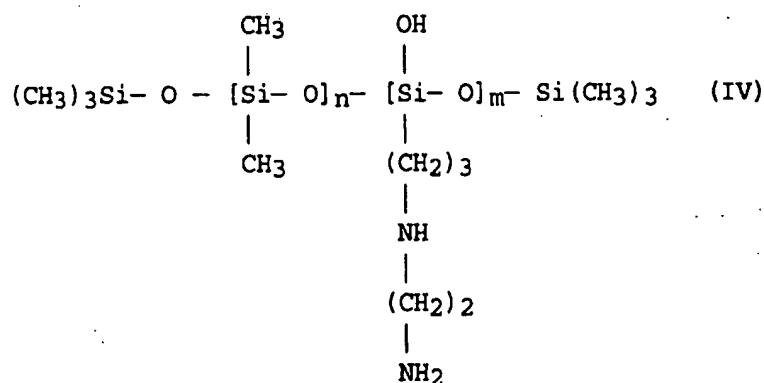


in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a monovalent radical of formula C<sub>q</sub>H<sub>2q</sub>L in which q is an integer from 2 to 8 and L is chosen from the groups



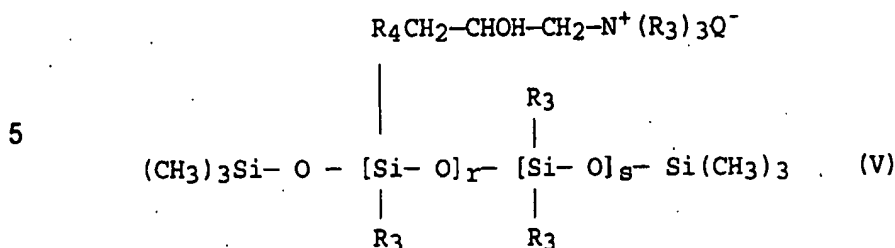
in which R<sub>2</sub> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A<sup>-</sup> denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



10 where  $\text{R}^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $\text{R}_4$  denotes a hydrocarbon radical, preferably a  $\text{C}_1 - \text{C}_{18}$  alkylene radical or a  $\text{C}_1 - \text{C}_{18}$ , and more preferably  $\text{C}_1 - \text{C}_8$ , alkyleneoxy radical;  $\text{Q}^-$  is a halide ion, preferably chloride;  $r$  denotes an average statistical value from 2 to 20, preferably from 2 to  
 15 8;  $s$  denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to  
 20 Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive, though not exclusive, listing of suitable silicone  
 25 compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at  $25^\circ\text{C}$  of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein  
 30 can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are  
 35 General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about

1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl<sup>TM</sup> from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit  $(\text{CH}_3)_3\text{SiO}_{1.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

#### Nonionic Polymer

Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.



Polyalkylene Glycols

These compounds are particularly useful for compositions which are designed to impart a soft, moist feeling to the hair. When present, the polyalkylene glycol is typically used at a level from about 0.025% to about 1.5%, preferably from about 0.05% to about 1%, and more preferably from about 0.1% to about 0.5% of the compositions.

The polyalkylene glycols are characterized by the general formula:



wherein R is selected from the group consisting of H, methyl, and mixtures thereof. When R is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols.

When R is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, n has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.

Polyethylene glycol polymers useful herein are PEG-2M wherein R equals H and n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R equals H and n has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R equals H and n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R equals H and n has an average value of about 9,000 (PEG 9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R equals H and n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

## FIXATIVE POLYMERS

Compositions herein may include a fixative polymer. The fixative polymers useful herein are those which provide a styling or setting benefit to the hair, including amphoteric fixative polymers, anionic fixative polymers, cationic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers. The fixative polymers in this section can be distinguished from the conditioning agent polymers mentioned above and the suspending agent polymers as mentioned below, in that they have a film-forming characteristic, and that the 3% aqueous solution of fixative polymers herein provide a viscosity of no more than about 2,000 cps.

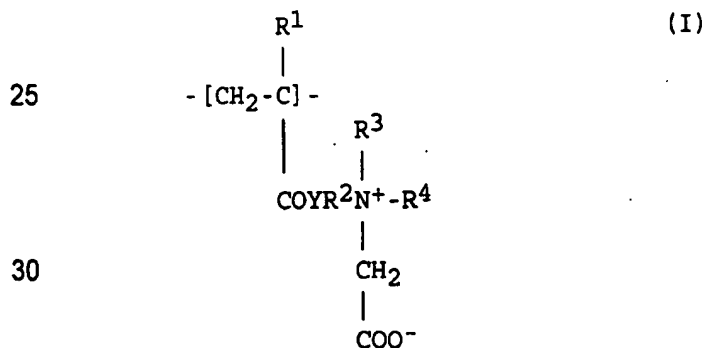
The fixative polymers, when present, are preferably included at a level of from about 0.01% to about 10% by weight of the composition. When two or more fixative polymers are used, each fixative polymer does not exceed about 5% by weight of the composition.

### Amphoteric Fixative Polymer

The amphoteric fixative polymers useful herein include betainized amphoteric fixative polymers as described in (1) and (2) below, and non-betainized fixative polymers as described in (3) and (4) below.

#### Betainized Amphoteric Fixative Polymers

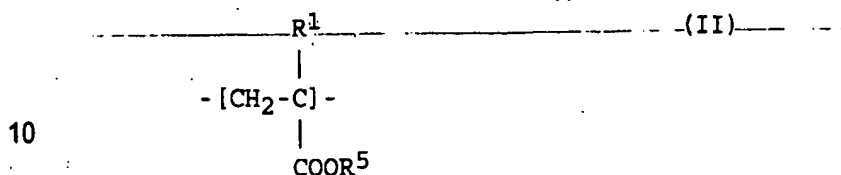
(1) Useful herein are polymers of betainized dialkylaminoalkyl (meth)acrylate or dialkylaminoalkyl (meth)acrylamide containing at least units of the formula:



wherein  $\text{R}^1$  denotes a hydrogen atom or a methyl group,  $\text{R}^2$  denotes an alkylene group having 1 to 4 carbon atoms, Y denotes O or -NH- and  $\text{R}^3$  and  $\text{R}^4$  independently of one another denote hydrogen or alkyl having 1 to 4 carbon atoms, and one cationic derivative consisting of a cationic surfactant containing at least one nitrogen atom joined to one or more fatty chains and optionally quaternised, or consisting of a cationic polymer of the polyamine,

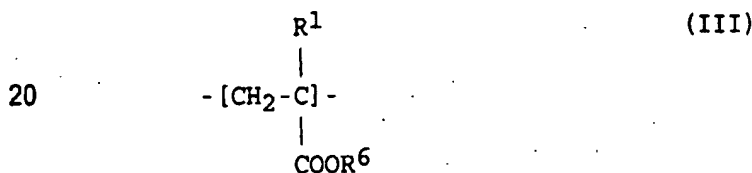
polyaminopolyamide or poly-(quaternary ammonium) type, the amine or ammonium groups forming part of the polymer chain or being joined thereto. These polymers usually have a molecular weight of 500 to 2,000,000.

The amphoteric polymers containing units corresponding to the above formula (I) are generally in the form of copolymers which contain, in addition to the units of the above mentioned formula (I), at least units of the formula:



wherein  $\text{R}^1$  is as defined above and  $\text{R}^5$  represents an alkyl or alkenyl radical having from 4 to 24 carbon atoms or a cycloalkyl radical having from 4 to 24 carbon atoms.

It is also possible to use terpolymers, tetrapolymers or pentapolymers which contain, in addition to the units (I) and (II) defined above, units of the formula:

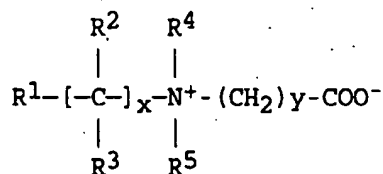


wherein  $\text{R}^6$  preferably denotes an alkyl or alkenyl group having 1 to 3 carbon atoms and  $\text{R}^1$  is as defined above.

The units of the formula (I) are preferably present in an amount of 25 to 45% by weight, units of the formula (II) are preferably present in an amount of 5 to 65% by weight, and units of the formula (III) are preferably present in an amount up to 50% by weight, relative to the total weight of the polymer.

A particularly preferred polymer is the copolymer containing units of the formulae (I), (II) and (III) in which Y denotes an oxygen atom,  $\text{R}^2$  denotes the group  $-\text{C}_2\text{H}_4-$ ,  $\text{R}^1$ ,  $\text{R}^3$  and  $\text{R}^4$  denote methyl,  $\text{R}^5$  denotes an alkyl group having 4 to 18 carbon atoms and  $\text{R}^6$  denotes an alkyl group having 1 to 3 carbon atoms. The average molecular weight of this polymer is preferably from 50,000 to 100,000. This polymer is sold under the trademark "Yukaformer" or "Diaformer" supplied by Mitsubishi Chemical Corporation.

(2) Useful herein are the betainized polymers containing zwitterionic units derived from the formula:



wherein R<sup>1</sup> denotes a polymerisable unsaturated group, such as an acrylate, methacrylate, acrylamide or methacrylamide group, x and y independently represent an integer from 1 to 3, R<sup>2</sup> and R<sup>3</sup> independently represent hydrogen, methyl, ethyl or propyl, and R<sup>4</sup> and R<sup>5</sup> independently represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R<sup>4</sup> and R<sup>5</sup> does not exceed 10.

Highly preferred betainized amphoteric polymers include commercially available material such as YUKAFORMER SM, YUKAFORMER FH, YUKAFORMER 301, YUKAFORMER 204WL, YUKAFORMER 510, YUKAFORMER M-75, YUKAFORMER R250S, Diaformer Z-SM, and Diaformer Z-W supplied by Mitsubishi Chemical Corporation.

#### Non-betainized Amphoteric Fixative Polymers

(3) Useful herein are the non-betainized amphoteric polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and -acrylamides.

(4) Useful herein are the non-betainized amphoteric polymers containing units derived from

- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quarternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

Highly preferred non-betainized amphoteric polymers include commercially available material such as octylacrylamine/acrylates/butylaminoethyl methacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

#### Cationic Fixative Polymer

The cationic fixative polymers useful herein are:

(1) Vinylpyrrolidone / quaternized dialkylaminoalkyl acrylate or methacrylate copolymers such as those sold under the tradename Gafquat 734 and 755N by the Gaf Corp.

(2) Cellulose ether derivatives containing quaternary ammonium groups.

(3) Cationic polysaccharides.

(4) Cationic polymers chosen from the group comprising:

i) polymers containing units of the formula:



wherein A denotes a radical containing two amino groups, preferably a piperaziny radical, and Z<sup>1</sup> and Z<sup>2</sup> independently denote a divalent radical which is a straight-chain or branched-chain alkylene radical which contains up to about 7 carbon atoms in the main chain, is unsubstituted or substituted by one or more hydroxyl groups and can also contain one or more oxygen, nitrogen and sulphur atoms and 1 to 3 aromatic and/or heterocyclic rings, the oxygen, nitrogen and sulphur atoms generally being present in the form of an ether or thioether, sulfoxide, sulphone, sulphonium, amine, alkylamine, alkenylamine, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane group;

ii) polymers containing units of the formula:



wherein A denotes a radical containing two amino groups, preferably a piperaziny radical, and Z' denotes the symbol Z<sup>3</sup> and Z<sup>4</sup> while denoting the symbol Z<sup>4</sup> at least once; Z<sup>3</sup> denotes a divalent radical which is a straight-chain or branched-chain alkylene or hydroxyalkylene radical having up to about 7 carbon atoms in the main chain, and Z<sup>4</sup> is a divalent radical which is a straight-chain or branched-chain alkylene radical which has up to about 7 carbon atoms in the main chain, is unsubstituted and substituted by one or more hydroxyl radicals and is interrupted by one or more nitrogen atoms, the nitrogen atom being substituted by an alkyl chain having from 1 to 4 carbon atoms, preferably 4 carbon atoms, which is optionally interrupted by an oxygen atom and optionally contains one or more hydroxyl groups; and

iii) the alkylation products, with alkyl and benzyl halides of 1 to 6 carbon atoms, alkyl tosylates or mesylates, and the oxidation products, of the polymers of the formulae (I) and (II) indicated above under i) and ii).

(5) Polyamino-polyamides prepared by the polycondensation of an acid compound with a polyamine. The acid compound can be organic dicarboxylic acids, aliphatic monocarboxylic and dicarboxylic acids containing a double bond, esters of the abovementioned acids, preferably the esters with lower alkanols having from 1 to 6 carbon atoms, and mixtures thereof. The polyamine is a bis-primary or mono- or bis-secondary polyalkylene-polyamine wherein up to 40 mol% of this polyamine can be a bis-primary amine, preferably ethylenediamine, or a bis-secondary amine, preferably piperazine, and up to 20 mol% can be hexamethylenediamine.

(6) The above mentioned polyamino-polyamides can be alkylated and/or crosslinked. The alkylation can be carried out with glycidol, ethylene oxide, propylene oxide or acrylamide. The crosslinking is carried out by means of a crosslinking agent such as:

- i) epihalogenohydrins, diepoxides, dianhydrides, unsaturated anhydrides and bis-saturated derivatives, in proportions of 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino-polyamide;
- ii) bis-halogenohydrins, bis-azetidinium compounds, bishalogeno acyldiamines and bis-(alkyl halides);
- iii) oligomers obtained by reacting a compound chosen from the group comprising bis-halogenohydrins, bis-azetidinium compounds, bis-

halogenoacyl-diamines, bis-(alkyl halides), epihalogenohydrins, diepoxides and bis-unsaturated derivatives, with another compound which is a difunctional compound which is reactive towards the compound; and

- 5 iv) the quaternisation product of a compound chosen from the compounds ii) and the oligomers iii) and containing one or more tertiary amine groups which can be totally or partially alkylated with an alkylating agent preferably chosen from methyl or ethyl chlorides, bromides, iodides, sulphates, mesylates and tosylates, benzyl chloride or  
10 bromide, ethylene oxide, propylene oxide and glycidol, the crosslinking being carried out by means of 0.025 to 0.35 mol, in particular of 0.025 to 0.2 mol and more particularly of 0.025 to 0.1 mol, of crosslinking agent per amine group of the polyamino-polyamide.

(7) Polyamino-polyamide derivatives resulting from the condensation of a  
15 polyalkylene-polyamine with a polycarboxylic acid, followed by alkylation by means of difunctional agents, such as the adipic acid/dialkylaminohydroxyalkyl-dialkylenetriamine copolymers in which the alkyl radical contains 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl.

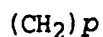
Useful polymers are adipic acid/dimethylaminohydroxypropyl-  
20 diethylenetriamine copolymers sold under the name Cartaretine F, F<sup>4</sup> or F<sup>8</sup> by SANDOZ.

(8) Polymers obtained by reacting polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group, with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic  
25 acids having 3 to 8 carbon atoms, the molar ratio of the polyalkylene-polyamine to the dicarboxylic acid being from 0.8:1 to 1.4:1, and the resulting polyamide being reacted with epichlorohydrin in a molar ratio of epichlorohydrin to the secondary amine groups of the polyamide of from 0.5:1 to 1.8:1.

Useful polymers are those sold under the name HERCOSETT 57 by  
30 Hercules Incorporated, and that sold under the name PD 170 or DELSETTE 101 by Hercules.

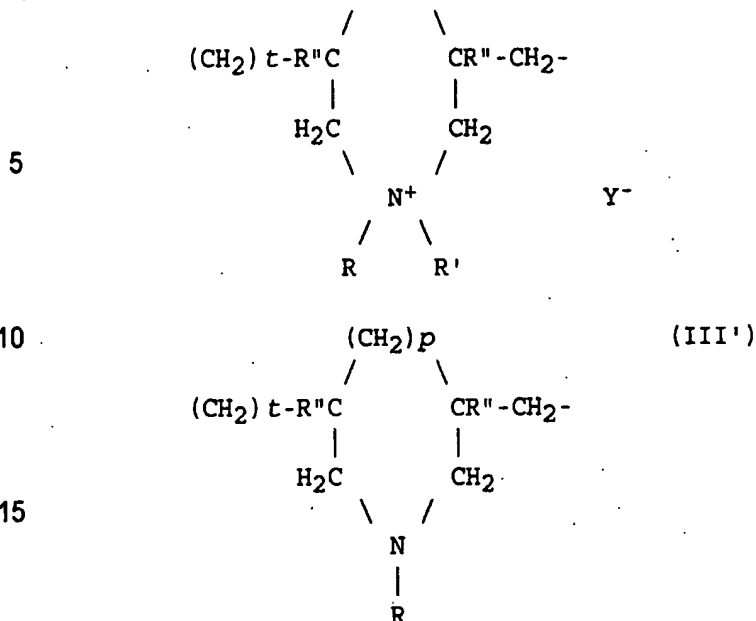
(9) Cyclic polymers generally having a molecular weight of 20,000 to 3,000,000 such as homopolymers containing, as the main constituent of the chain, units corresponding to the formula (III) or (III')

35



(III)

54

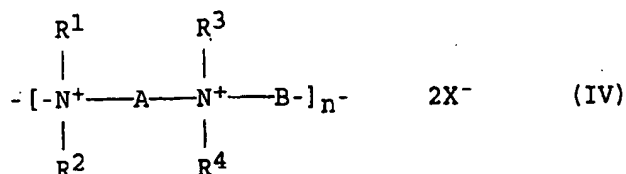


20 in which  $p$  and  $t$  are 0 or 1, and  $p+t=1$ ,  $R''$  denotes hydrogen or methyl,  $R$  and  $R'$  independently of one another denote an alkyl group having from 1 to 22 carbon atoms, a hydroxylalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, or a lower amidoalkyl group, and  $R$  and  $R'$  can denote, together with the nitrogen atom to which they are attached, heterocyclic groups such as piperidinyl or morpholinyl, and  $Y$  is bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. Copolymers containing units of the formula III and III' may also contain units derived from acrylamide or from diacetoneacrylamide.

30 Amongst the quaternary ammonium polymers of the type defined above, those which are preferred are the dimethyldiallylammonium chloride homopolymer sold under the name MERQUAT 100 and having a molecular weight of less than 100,000, and the dimethyldiallylammonium chloride/acrylamide copolymer having a molecular weight of more than 500,000 and sold under the name MERQUAT 550 by CALGON Corporation.

(10) Poly-(quaternary ammonium) compounds of the formula





wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently aliphatic, alicyclic or arylaliphatic radicals containing a maximum of 20 carbon atoms, or lower hydroxyaliphatic radicals, or alternatively, with the nitrogen atoms to which they are attached, heterocyclic rings optionally containing a second hetero-atom other than nitrogen, or alternatively R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> represent a group CH<sub>2</sub>CHR<sup>3</sup>R<sup>4</sup> wherein R<sup>3</sup> denoting hydrogen or lower alkyl and R<sup>4</sup> denoting SO, CN, CON(R<sup>6</sup>)<sub>2</sub>, COOR<sup>5</sup>, COR<sup>5</sup>, COOR<sup>7</sup>D, or CONHR<sup>7</sup>D; R<sup>5</sup> denoting lower alkyl, R<sup>6</sup> denoting hydrogen or lower alkyl, R<sup>7</sup> denoting alkylene and D denoting a quaternary ammonium group; A and B independently represent a polymethylene group containing from 2 to 20 carbon atoms, which can be linear or branched, saturated or unsaturated and can contain, inserted in the main chain one or more groups -CH<sub>2</sub>-Y-CH<sub>2</sub>- wherein Y denotes benzene, oxygen, sulfur, SO, SO<sub>2</sub>, SS, NR<sup>8</sup>, N<sup>+</sup>(R<sup>9</sup>)<sub>2</sub>X<sup>1-</sup>, CHOH, NHCONH, CONR<sup>8</sup>, or COO; X<sup>1-</sup> denoting an anion derived from a mineral or organic acid, R<sup>8</sup> denoting hydrogen or lower alkyl and R<sup>9</sup> denoting lower alkyl, or alternatively A and R<sup>1</sup> and R<sup>3</sup> form a piperazine ring with the two nitrogen atoms to which they are attached. If A denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B can also denote a group: -(CH<sub>2</sub>)<sub>n</sub>-CO-D-OC-(CH<sub>2</sub>)<sub>n</sub>-; wherein n is selected so that the molecular weight is generally between 1,000 and 100,000; and D denotes:

i) a glycol radical of the formula -O-Z-O-, in which Z denotes a linear or branched hydrocarbon radical or a group corresponding to the formulae:

-[CH<sub>2</sub>-CH<sub>2</sub>-O]<sub>x</sub>-CH<sub>2</sub>-CH<sub>2</sub>- or -[CH<sub>2</sub>-C(CH<sub>3</sub>)H-O]<sub>y</sub>-CH<sub>2</sub>-C(CH<sub>3</sub>)H- wherein x and y denote an integer from 1 to 4, representing a definite and unique degree of polymerisation;

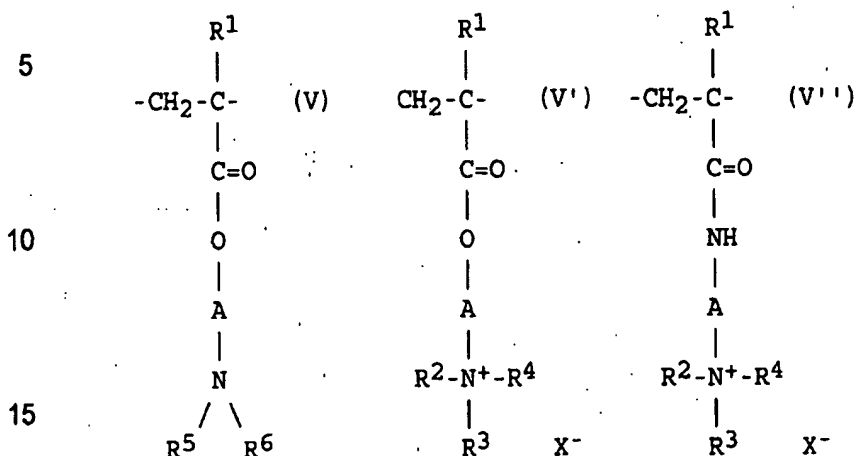
ii) a bis-secondary diamine radical, such as a piperazine derivative;

iii) a bis-primary diamine radical of the formula: -N-H-Y-NH-, in which Y denotes a linear or branched hydrocarbon radical or the divalent radical

-CH<sub>2</sub>-CH<sub>2</sub>-S-S-CH<sub>2</sub>-CH<sub>2</sub>-; or

iv) a ureylene group of the formula -N-H-CO-NH-.

(11) Homopolymers or copolymers derived from acrylic or methacrylic acid and containing at least one unit:



wherein  $\text{R}^1$  is H or  $\text{CH}_3$ , A is a linear or branched alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 1 to 4 carbon atoms,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  independently denote an alkyl group having 1 to 18 carbon atoms or a benzyl group,  $\text{R}^5$  and  $\text{R}^6$  denote H or alkyl having 1 to 6 carbon atoms and X denotes methosulphate or halide, such as chloride or bromide.

The comonomer or comonomers which can be used typically belong to the family comprising: acrylamide, methacrylamide, diacetone-acrylamide, acrylamide and methacrylamide substituted on the nitrogen by one or more lower alkyls, alkyl esters of acrylic and methacrylic acids, vinylpyrrolidone and vinyl esters.

Useful polymers are Quaternium 38, 37, 49 and 42 in the CTFA, acrylamide/beta-methacryloyloxyethyl-trime-thylammonium methosulphate copolymers sold under the names Teten 205,210,220 and 240 by Hercules, and aminoethylacrylate phosphate/acrylate copolymer sold under the name Catrex by National Starch & Chemicals, and the crosslinked graft cationic copolymers having a molecular weight of 10,000 to 1,000,000, and preferably of 15,000 to 500,000, and resulting from the copolymerisation of: at least one cosmetic monomer, dimethylaminoethyl methacrylate, polyethylene glycol and a polyunsaturated crosslinking agent, such as those mentioned in the CTFA dictionary under the name AMODIMETHICONE, such as the product marketed as a mixture with other ingredients under the name DOW CORNING 929 cationic emulsion.

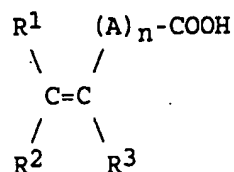
(12) Other cationic polymers which can be used are polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine units or vinylpyridinium units in the chain, condensates of polyamines and of epichlorohydrin, poly-(quaternary ureylenes) and chitin derivatives.

Highly preferred cationic fixative polymers include commercially available material such as Polyquaternium 4 under the tradenames CELQUAT H100 and CELQUAT L200 supplied by National Starch & Chemicals, and Polyquaternium 11 under the tradename GAFQUAT 755N supplied by ISP.

#### Anionic Fixative Polymer

The anionic fixative polymers useful herein include polymers containing units derived from carboxylic, sulphonic or phosphoric acid and usually have a molecular weight of 500 to 5,000,000. These polymers are water-soluble polymers, it being possible for this solubility to be obtained by neutralisation.

The carboxylic acid groups can be provided by unsaturated monocarboxylic or dicarboxylic acids, such as those corresponding to the formula:



wherein n is 0 or an integer from 1 to 10, A denotes a methylene group optionally joined to the carbon atom of the saturated group, or to the adjacent methylene group in the case where n is greater than 1, via a heteroatom, such as oxygen or sulphur, R<sup>1</sup> denotes a hydrogen atom or a phenyl or benzyl group, R<sup>2</sup> denotes a hydrogen atom, a lower alkyl group or a carboxyl group and R<sup>3</sup> denotes a hydrogen atom, a lower alkyl group, CH<sub>2</sub>COOH, or a phenyl or benzyl group.

According to the invention, the preferred polymers containing carboxylic acid groups are:

(1) Homopolymers or copolymers of acrylic or methacrylic acid or salts thereof, and in particular, the products sold under the name VERSICOL E or K, and ULTRAHOLD by BASF and under the name DARVAN No. 7 by Van der Bilt; acrylic acid/acrylamide copolymers sold in the form of their sodium salt under the name RETEN 421, 423 or 425 by HERCULES; and the sodium salts of polyhydroxycarboxylic acids, sold under the name HYDAGEN F by HENKEL.

(2) Copolymers of acrylic or methacrylic acid with a monoethylenic monomer, such as ethylene, styrene, a vinyl or allyl ester or acrylic or methacrylic acid ester, optionally grafted onto a polyalkylene glycol, such as polyethylene glycol, and optionally crosslinked. Other such copolymers contain an optionally  
5 N-alkylated and/or N-hydroxylated acrylamide unit in their chain, such as those sold under the name QUADRAMER 5 by American Cyanamid.

(3) Copolymers derived from crotonic acid, such as those containing, in their chain, vinyl acetate or propionate units and optionally other monomers such as allyl or methallyl esters, a vinyl ether or a vinyl ester of a saturated linear or  
10 branched carboxylic acid with a hydrocarbon chain of at least 5 carbon atoms, if appropriate, for these polymers to be grafted and crosslinked, or also a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. Included in this class are those with the tradename RESYN 28-2930, 28-2913, and 28-1310 sold by National Starch & Chemicals.

(4) Polymers derived from maleic, fumaric and itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, such as those sold under the name GANTREZ A, SP, and ES by ISP. Other polymers included in this class are copolymers of maleic,  
15 citraconic and itaconic anhydrides with an allyl or methallyl ester optionally containing an acrylamido or methacrylamido group, or with an  $\alpha$ -olefine, acrylic or methacrylic acid ester, acrylic or methacrylic acid or vinylpyrrolidone unit in their chain; the anhydride groups can be monoesterified or monoamidified.

(5) Polyacrylamides containing carboxylate groups. Polymers comprising sulphonic groups include polymers containing vinylsulphonic, styrenesulphonic,  
25 lignosulphonic or naphthalenesulphonic units. These polymers are chosen, in particular, from amongst:

- i) Polyvinylsulphonic acid salts having a molecular weight of 1,000 to 100,000, and also copolymers with an unsaturated comonomer, such as acrylic or methacrylic acid or an ester thereof and also substituted  
30 or unsubstituted acrylamide or methacrylamide, vinyl esters, vinyl ethers and vinylpyrrolidone.
- ii) Polystyrenesulphonic acid salts, such as the sodium salt sold by National Starch & Chemicals under the name Flexan 500 and 130.
- iii) Alkali metal or alkaline earth metal salts of sulphonic acids derived  
35 from lignin, and more particularly calcium lignosulphonates or sodium lignosulphonates, such as the product sold under the name

Marasperse C-21 by American Can Co. and the C<sub>10</sub> to C<sub>14</sub> products sold by Avebene.

- iv) Polymers containing salified alkylnaphthalenesulphonic acid units, such as the sodium salt under the name Darvan No. 1 by Van der Bilt.

5 The anionic hair fixative polymers herein which include anionic monomers are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. In the compositions the neutralisation of a polymer may be achieved by use of an inorganic base, preferably KOH. However organic base, preferably AMP (amino methyl propanol) and mixture of inorganic and organic base may also be used to effect the desired level of neutralisation in hair styling compositions. In total from about 50% to about 100%, preferably from about 70% to about 100%, most preferably from about 80% to about 100% of the acidic monomers of each polymer utilised should be neutralised with base.

10 Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers provided they are utilised as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols are suitable neutralisers.

Examples of suitable organic neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1, 3-propanediol (AMPD), 2-amino-2ethyl-1, 3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethylsteramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

25 Preferred neutralising agents for use in hair care compositions of the present invention are potassium and sodium hydroxides.

Highly preferred anionic fixative polymers include commercially available material such as vinyl acetate/crotonic acid/vinyl neodecanoate copolymers and vinyl acetate/crotonic acid copolymers with the tradenames RESYN 28-2930, RESYN 28-2913, and RESYN 28-1310 supplied by National Starch & Chemicals, and acrylates copolymers and acrylates/acrylamide copolymers with tradenames LUVIMER 100P, ULTRAHOLD 8, and ULTRAHOLD STRONG supplied by BASF Corporation.

35 Nonionic Fixative Polymers

Nonionic fixative polymers useful herein are homopolymer of vinylpyrrolidone or vinylcaprolactum and copolymers of vinylpyrrolidone with vinylacetate such as those with tradenames LUVISKOL K grades and LUVISKOL VA grades supplied by BASF Corporation.

5 Silicone Grafted Copolymers

The silicone grafted copolymers useful herein include those which have a vinyl polymeric backbone (A and B monomers), and grafted to such backbone a polydimethylsiloxane macromer (C macromer) having a weight average molecular weight of from about 1,000 to about 50,000. Preferably, these  
10 copolymers contain from and from about 50.0% to about 99.9% of the combination of A and B monomers, and from about 0.1% to about 50.0% of C macromer, wherein A is a lipophilic, low polarity free radically polymerizable vinyl monomer, such as methacrylic or acrylic esters; B is a hydrophilic polar monomer which is copolymerizable with A, such as acrylic acid, N,N-dimethylacrylamide,  
15 dimethylaminoethylmethacrylate, diallyldimethylammonium chloride, vinyl pyrrolidone, or quaternized dimethylaminoethyl methacrylate; and C is a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, based on polydimethylsiloxane. Preferred silicone grafted copolymers are those having a Tg above about -20°C, and a molecular weight of  
20 from about 10,000 to about 1,000,000.

Suitable silicone grafted copolymers herein include those listed below wherein the numbers indicate the weight ratio of monomers and macromers in the copolymer, silicone macromer S1 is a dimethylpolysiloxane having a molecular weight of about 20,000, and silicone macromer S2 is a  
25 dimethylpolysiloxane having a molecular weight of about 10,000.

- 1) 20/63/17 acrylic acid/t-butyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 100,000
- 2) 10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 400,000
- 30 3) 60/20/20 diallyldimethyl ammonium methacrylate/isobutyl methoacrylate /silicone macromer S2, having a copolymer molecular weight about 500,000
- 4) 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 400,000
- 35 5) 10/70/20 acrylic acid/t-butyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000

- 6) 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, having a copolymer molecular weight about 200,000
- 7) 60/25/15 N,N'-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 200,000
- 5 8) 12/64/4/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000
- 9) 30/40/10/20 N,N'-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/silicone macromer S1, having a copolymer molecular weight about 300,000
- 10 10) 80/20 t-butylacrylate/silicone macromer S2, having a copolymer molecular weight about 150,000

#### SCATTERING PARTICLE

- 15 In another aspect of the present invention, the hair care composition of the present invention comprises a scattering particle having an average particle size of at least about 0.03 $\mu$ m, preferably from about 0.03 $\mu$ m to about 50 $\mu$ m, more preferably from about 0.1 $\mu$ m to about 50 $\mu$ m. The scattering particle can be any compound which is compatible, stable, and safe to use in a hair care composition, so long as they meet the required particle size as explained above.
- 20 The size of the particles are selected as such that they provide effective multiple light scattering, thereby prolonging the path of UV light radiation. Therefore, these scattering particles enhance the UV light absorbency of the optical brighteners. Hair care compositions comprising a combination of optical brighteners and scattering particles provide effective UV light protection.
- 25 Preferably, the scattering particles of the present invention are included at a level of from about 0.01% to about 20%, more preferably from about 0.05% to about 15% of the hair care composition.

- 30 Scattering particles useful herein include silicones, oils, antimicrobial agents, crystalline suspending agents, metal oxides, and mixtures thereof. It is understood by one skilled in the art that these compounds may provide not only UV light scattering benefits, but also other benefits due to the characteristic of the compound. For example, silicones and oils may provide hair conditioning benefits, and metal oxides may provide aesthetic benefits.

#### Silicone Scattering Particles

Silicone scattering particles useful herein include any silicone compound as described above under the section for conditioning agent, so long as it has the required particle size.

- Commercially available silicone scattering particles suitable herein include
- 5 Silicone emulsion SM2169 available from G. E. having an average particle size of about 0.25 $\mu$ m, Silicone blend SE76 available from G. E. having an average particle size of about 15 $\mu$ m, Silicone emulsion X65-4829 available from Toshiba Silicone having an average particle size of about 0.5 $\mu$ m, and 15/85 Silicone blend available from Shinetsu having an average particle size of from about 10 $\mu$ m to about 30 $\mu$ m.

#### Oil Scattering Particles

- Oil scattering particles useful herein include those which have a melting point of not more than about 25°C, and have the required particle size. The oils may be volatile or non-volatile. Some oils may be the same compounds as those
- 15 described above under the section for conditioning agents.

Oils useful herein include fatty acids, fatty acid derivatives, and hydrocarbons.

- The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more
- 20 preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

- The fatty acid derivatives include, for example, methyl linoleate, ethyl
- 25 linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol
- 30 tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

- The hydrocarbons useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably
- 35 from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of



- alkenyl monomers, such as polymers of C<sub>2-6</sub> alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have
- 5 substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples
- 10 of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.
- 15 Commercially available oil scattering particles suitable herein include Mineral oil obtained by Amerchol having an average particle size from about 1 $\mu$ m to about 10 $\mu$ m.

#### Antimicrobial Agent Scattering Particle

- Antimicrobial agent scattering particles useful herein include
- 20 pyridinethione salts such as 1-hydroxy-2-pyridinethione salts of zinc, tin, caminium, magnesium, aluminium, and zirconium; selenium sulfide, sulfur, octopirox, and propyl paraben.

- Commercially available antimicrobial agent scattering particles suitable herein include zinc pyridinethione available from Olin having an average particle
- 25 size of about 5 $\mu$ m.

#### Crystalline Suspending Agent Scattering Particle

- Crystalline suspending agent scattering particles herein include acyl derivatives, alkanol amides of fatty acids, and N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof. The acyl derivatives useful herein include
- 30 ethylene glycol stearates, both mono and distearate, long chain amine oxides such as alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide, and mixtures thereof. When used in the shampoo compositions, these preferred suspending agents are present in the composition in crystalline form. These suspending agents are described in U.S. Patent 4,741,855. Alkanol
- 35 amides of fatty acids useful herein include those having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred

examples of which include stearic monoethanolamide, cocomonethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof useful herein include sodium and potassium salts of

- 5 N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid.

Commercially available crystalline suspending agent scattering particles suitable herein include ethylene glycol distearate-with tradename EGDS available from Th. Goldschmidt AG having an average particle size of about 10 $\mu$ m.

#### Metal Oxide Scattering Particle

- 10 Metal oxide scattering particles useful herein include titanium dioxide, zinc oxide, chromium oxide, cobalt oxide, tin oxides, silicates, and alloy compounds thereof, micas, titanated micas, and clays such as montmorillonite, zeolite, beidellite, nontronite, saponite, vermiculite, kaolinite, and bentonite.

- 15 Commercially available metal oxide scattering particles suitable herein include titanated mica with tradename TimironMP-1005 available from Merck having an average particle size of about 15 $\mu$ m, and montmorillonite with tradename Southern Clay available from Gelwhite having an average particle size of from about 1 to about 10 $\mu$ m.

#### CARRIER

- 20 Compositions herein may include a carrier. The level and species of the carrier are selected according to the compatibility with other components, and desired characteristic of the product. For example, a high percentage of volatile solvents of low boiling point and/or propellant are suitably used for product forms aimed to be left on the hair. On the other hand, water solutions of volatile and
- 25 non-volatile solvents are suitably used for product forms aimed to be rinsed off the hair after washing or treating the hair with the product.

The carrier useful in the present invention include volatile solvents, non-volatile solvents, propellants, and mixtures thereof.

- 30 Volatile solvents useful herein include water, lower alkyl alcohols having from 1 to 3 carbons, and hydrocarbons having from about 5 to about 8 carbons. The preferred volatile solvents are water, ethanol, isopropanol, pentane, hexane, and heptane. The water useful herein include deionized water and water from natural sources containing mineral cations. Deionized water is preferred.

- 35 Non-volatile solvents useful herein include alkyl alcohols having more than 3 carbons, and polyhydric alcohols. The polyhydric alcohols useful herein include 1,2-propane diol or propylene glycol, 1,3-propane diol, hexylene glycol,

glycerin, diethylene glycol, dipropylene glycol, 1,2-butylene glycol, and 1,4-butylene glycol.

Propellants may be used for mousse and hair spray product forms. Propellants, when used in the present invention, are selected depending on variables such as the remainder of components, the package, and whether the product is designed to be used standing or invert.

Propellants useful herein include fluorohydrocarbons such as difluoroethane 152a available from DuPont, dimethylether, and hydrocarbons such as propane, isobutane, n-butane, mixture of hydrocarbons such as LPG (liquid petroleum gas), carbon dioxide, nitrous oxide, nitrogen, and compressed air.

#### ADDITIONAL COMPONENTS

The compositions of the present invention may include a variety of additional components, which may be selected by the artisan according to the desired characteristics of the final product. Additional components include, for example, polyvalent metal cations, and other additional components.

#### Polyvalent Metal Cations

Suitable polyvalent metal cations include divalent and trivalent metals, divalent metals being preferred. Exemplary metal cations include alkaline earth metals, such as magnesium, calcium, zinc, and copper, and trivalent metals such as aluminum and iron. Preferred are calcium and magnesium.

The polyvalent metal cation can be added as an inorganic salt, organic salt, or as a hydroxide. The polyvalent metal cation may also be added as a salt with anionic surfactants, as mentioned above.

Preferably, the polyvalent metal cation is introduced as an inorganic salt or organic salt. Inorganic salts include chloride, bromide, iodine, nitrate, or sulfate, more preferably chloride or sulfate. Organic salts include L-glutamate, lactate, malate, succinate, acetate, fumarate, L-glutamic acid hydrochloride, and tartarate.

It will be clear to those skilled in the art that, if polyvalent salts of the anionic surfactant is used as the mode of introducing the polyvalent metal cations into the compositions hereof, only a fraction of the anionic surfactant may be of polyvalent form, the remainder of the anionic surfactant being necessarily added in monovalent form.

Hardness of the conditioning shampoo compositions can be measured by standard methods in the art, such as by ethylene diamine tetraacetic acid (EDTA)

titration. In the event that the composition contains dyes or other color materials that interfere with the ability of EDTA titration to yield a perceptible color change, hardness should be determined from the composition in the absence of the interfering dye or color.

#### 5 Other Additional Components

A wide variety of other additional ingredients can be formulated into the present compositions. These include other conditioning agents such as hydrolyzed collagen with tradename Peptin 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; emulsifying surfactants for dispersing water insoluble components in the carrier; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate. Such optional ingredients generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

### EXAMPLES

25 The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

#### 30 Compositions

|  | Ex.1 | Ex.2 | Ex.3 | Ex.4 | Ex.5 | Ex.6 |
|--|------|------|------|------|------|------|
| Disodium-1,4-bis(2-sulfostyryl)biphenyl *1 | 0.50 | -    | -    | -    | -    | -    |

|   |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|
| 4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl) amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid *2 | -     | 0.80  | -     | -     | -     | -     |
| 4-methyl-7,7'-dihydroxycoumarin   | -     | -     | 0.50  | -     | -     | -     |
| 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene *3  | -     | -     | -     | 0.20  | -     | -     |
| 2-(4-styryl-3-sulfophenyl)-2H-naphtho[1,2-d]triazole  | -     | -     | -     | -     | 0.25  | -     |
| 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine *4  | -     | -     | -     | -     | -     | 0.50  |
| Mineral oil (1-10 $\mu$ m) *5   | 0.50  | -     | -     | -     | -     | -     |
| Silicone emulsion 1 (0.25 $\mu$ m) *6   | -     | 1.50  | -     | -     | -     | -     |
| Silicone blend (15 $\mu$ m) *7  | -     | -     | 2.00  | 2.00  | 2.00  | 2.00  |
| Ethylene Glycol Distearate (10 $\mu$ m) *8  | 2.00  | 2.00  | 2.00  | 2.00  | 2.00  | 2.00  |
| Titanated Mica (15 $\mu$ m) *9  | -     | -     | -     | 0.50  | -     | -     |
| Zinc pyridinethione (5 $\mu$ m) *10   | -     | -     | -     | -     | 0.25  | -     |
| Montmorillonite (1~10 $\mu$ m) *11  | 0.50  | -     | -     | -     | -     | 0.50  |
| Ammonium Laureth-3 Sulfate  | 10.00 | 12.00 | 10.00 | 10.00 | 10.00 | 10.00 |
| Ammonium Lauryl Sulfate   | -     | 2.00  | -     | 2.00  | 2.00  | 2.00  |
| N-acyl-L-glutamate Triethanolamine *12  | 4.00  | 2.00  | 2.00  | -     | -     | -     |
| Sodium Lauroyl Sarcosinate *13  | -     | -     | 2.00  | 2.00  | 2.00  | 2.00  |
| Laureth-20 *14  | -     | -     | 0.50  | -     | -     | -     |
| Cocamidopropylbetaine *15   | 4.00  | 2.00  | 2.00  | 2.00  | 2.00  | 2.00  |
| Alkyl polyglucoside *16   | -     | 1.00  | -     | 0.50  | 0.50  | 0.50  |
| Cocamide MEA  | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  |
| Fragrance   | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  |
| DMDM Hydantoin  | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  |
| Cetyl alcohol   | -     | -     | -     | 0.80  | 0.80  | 0.80  |
| Stearyl alcohol   | -     | -     | -     | 0.20  | 0.20  | 0.20  |

|                           |              |       |       |       |       |       |
|---------------------------|--------------|-------|-------|-------|-------|-------|
| Polyquaternium-10 *17     | 0.50         | 0.50  | 0.50  | 0.50  | 0.50  | 0.50  |
| Hydrolyzed Collagen *20   | 0.01         | -     | -     | -     | -     | -     |
| Vitamin E *21             | 0.01         | -     | -     | -     | -     | -     |
| Panthenol *22             | 0.025        | -     | -     | -     | -     | -     |
| Panthenyl Ethyl Ether *23 | 0.225        | -     | -     | -     | -     | -     |
| Monosodium phosphate      | 0-1.0        | 0-1.0 | 0-1.0 | 0-1.0 | 0-1.0 | 0-1.0 |
| Disodium phosphate        | 0-1.0        | 0-1.0 | 0-1.0 | 0-1.0 | 0-1.0 | 0-1.0 |
| Deionized Water           | q.s. to 100% |       |       |       |       |       |

|   | Ex. 7 | Ex.8 | Ex.9 | Ex.10 |
|---|-------|------|------|-------|
| Disodium-1,4-bis(2-sulfostyryl)biphenyl *1  | -     | 0.30 | 0.50 | -     |
| 4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl) amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid *2 | 0.80  | -    | -    | -     |
| 2-(4-styryl-3-sulfophenyl)-2H-naphto[1,2-d]triazole   | -     | -    | -    | 0.40  |
| 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene *3  | -     | -    | 0.20 | -     |
| Silicone Emulsion 2 ( 0.5 $\mu$ m) *18  | 0.20  | -    | -    | -     |
| Silicone Emulsion 1 (0.25 $\mu$ m) *6   | -     | 5.80 | -    | -     |
| Mineral oil (1-10 $\mu$ m) *5   | -     | 0.50 | -    | -     |
| 15/85 Silicone Blend (10-30 $\mu$ m) *19  | -     | -    | 4.20 | 4.20  |
| Titanated Mica (15 $\mu$ m) *9  | -     | -    | -    | 0.50  |
| Montmorillonite (1~10 $\mu$ m) *11  | -     | 0.50 | -    | -     |
| Zinc pyridinethione (5 $\mu$ m) *10   | -     | -    | 0.20 | -     |
| Aminomethylpropanol *24   | 0.60  | -    | -    | -     |
| Behenyl Alcohol *25   | 0.10  | -    | -    | -     |
| Carbomer *26  | 0.50  | 0.26 | -    | -     |
| Cetyl Alcohol *27   | 0.20  | -    | 2.50 | 2.50  |
| Cetyl Hydroxyethyl Cellulose *28  | -     | -    | -    | -     |
| Citric Acid *29   | -     | 0.10 | -    | -     |
| L-Glutamic Acid *30   | 0.08  | -    | 0.64 | 0.64  |
| Octyl Methoxycinnamate *31  | -     | 0.05 | -    | -     |
| Pentaerythritol Tetraisostearate *32  | 0.10  | -    | -    | -     |
| Polyoxyethylene stearyl ether *33   | -     | -    | 0.50 | -     |
| Polyoxyethylene Glycol *34  | 0.50  | -    | -    | 0.20  |

|                                       |              |      |      |      |
|---------------------------------------|--------------|------|------|------|
| Polyquaternium-10 *17                 | 1.00         | -    | -    | 0.20 |
| Stearamidopropyl dimethylamine *35    | 0.20         | -    | 2.00 | 2.00 |
| Stearyl Alcohol *36                   | 0.20         | 3.00 | 4.50 | 4.50 |
| Trimethylolpropane Triisostearate *37 | -            | -    | -    | 0.25 |
| Trimethylolpropane Trioleate *38      | 0.10         | -    | -    | -    |
| Preservatives                         | -            | 0.65 | -    | 0.53 |
| Perfume                               | 0.08         | 0.15 | 0.20 | 0.20 |
| Deionized Water                       | q.s. to 100% |      |      |      |

### Definitions

- \*1 Disodium-1,4-bis(2-sulfostyryl)biphenyl : Tinopal CBS-X available from Ciba Geigy
- 5 \*2 4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl) amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid : Tinopal UNPA-GX available from Ciba Geigy
- \*3 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene : 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene available from TCI
- 10 \*4 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine : 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine available from Ciba Geigy
- \*5 Mineral oil (1-10  $\mu\text{m}$ ) : Mineral oil (1-10  $\mu\text{m}$ ) available from Amerchol
- \*6 Silicone emulsion ( 0.25  $\mu\text{m}$ ) : SM2169 available from G.E.
- \*7 Silicone blend (15  $\mu\text{m}$ ) : SE76 available from G.E.
- 15 \*8 Ethylene Glycol Distearate (10  $\mu\text{m}$ ) : EGDS available from Th. Goldschmidt AG
- \*9 Titanated Mica (15  $\mu\text{m}$ ) : TimironMP-1005 available from Merck
- \*10 Zinc pyridinethione (5  $\mu\text{m}$ ) : Zinc pyridinethione (5  $\mu\text{m}$ ) available from Olin
- \*11 Montmorillonite (1~10  $\mu\text{m}$ ) : Southern Clay available from Gelwhite
- 20 \*12 N-acyl-L-glutamate Triethanolamine : CT12S available from Ajinomoto
- \*13 Sodium Lauroyl Sarcosinate : Soypon available from Kawaken Fine Chem.
- \*14 Laureth-20 : BL-20 available from Nikko
- \*15 Cocamidopropylbetaine : Tegobetain available from Th.Goldschmidt AG
- 25 \*16 Alkyl polyglucoside : Plantacare 2000UP available from Henkel
- \*17 Polyquaternium-10 : UCARE Polymer LR 400 available from Amerchol
- \*18 Silicone Emulsion ( 0.5  $\mu\text{m}$ ) : X65-4829 available from Tosil/GE
- \*19 15/85 Silicone Blend (10-30  $\mu\text{m}$ ) : available from Shinetsu

- \*20 Hydrolyzed Collagen: Peptin 2000 available from Hormel
  - \*21 Vitamin E: Emix-d available from Eisai
  - \*22 Panthenol: available from Roche
  - \*23 Panthenyl Ethyl Ether : available from Roche
  - 5 \*24 Aminomethylpropanol : AMP-regular available from Angus
  - \*25 Behenyl Alcohol : 1-Docosanol ( 97%) available from Wako
  - \*26 Carbomer : Carbopol 980 available from BF Goodrich
  - \*27 Cetyl Alcohol : Konol series available from Shinihon Rika
  - \*28 Cetyl Hydroxyethyl Cellulose : Polysurf 67 available from Aqualon
  - 10 \*29 Citric Acid : Anhydrous Citric acid available from Haarmann & Reimer
  - \*30 L-Glutamic Acid : L-Glutamic acid (cosmetic grade) available from Ajinomoto
  - \*31 Octyl Methoxycinnamate : Octyl Methoxycinnamate available from ISP
  - \*32 Pentaerythritol Tetraisostearate : KAK PTI available from Kokyu alcohol
  - 15 \*33 Polyoxyethylene stearyl ether : Brij-721 available from ICI
  - \*34 Polyoxyethylene Glycol : WSR N-10 available from Amerchol
  - \*35 Stearamidopropyl dimethylamine : Amidoamine MPS available from Nikko
  - \*36 Stearyl Alcohol : Konol series available from Shinihon Rika
  - \*37 Trimethylolpropane Triisostearate : KAK TTI available from Kokyu alcohol
  - 20 \*38 Trimethylolpropane Trioleate : Enujerubu TP3SO available from Shinihon
- Method of Preparation

The compositions of Examples 1 through 10 as shown above can be prepared by any conventional method well known in the art. Suitable methods are described below.

- 25       The shampoo compositions of Examples 1 through 6 can be suitably prepared as follows: polymer and surfactants are dispersed in water to form a homogenous mixture. To this mixture are added the other ingredients except for silicone emulsion (if present), perfume, and salt; the obtained mixture is agitated. If present, the silicone emulsion is made with Dimethicone, a small amount of
- 30       detergent surfactant, and a portion of water. The obtained mixture is then passed through a heat exchanger to cool, and the silicone emulsion, perfume, and salt are added. The obtained compositions are poured into bottles to make hair shampoo compositions.

- 35       Alternatively, water and surfactants and any other solids that need to be melted can be mixed together at elevated temperature, e.g., above about 70°C, to speed the mixing into shampoo. Additional ingredients can be added either to



this hot premix or after cooling the premix. The ingredients are mixed thoroughly at the elevated temperature and then pumped through a high shear mill and then through a heat exchanger to cool them to ambient temperature. If present in the composition, silicone emulsified at room temperature in concentrated surfactant is added to the cooled mix.

The conditioning hair sprays, lotions and conditioners of Examples 7 through 10 are suitably made as follows: If included in the formula, polymeric materials are dispersed in water at room temperature. If required, the polymeric materials such as Carbomer and Acrylates/Steareth-20 Methacrylate Copolymer may be neutralized after dispersing. The mixture is then heated up to above 60°C, and fatty alcohols and emulsifiers are added if included in the formulation. After cooling down to below 50°C, the remaining components are added with agitation then cooled down to about 30°C. Ethanol is added here if included in the formula. A triblender and mill can be used if necessary to disperse the materials. As appropriate, the mixture thus obtained can be packed into an aerosol can with propellant.

Examples 1 through 10 have many advantages. For example, they can be used daily, and provide color alteration, shininess, and UV protection to the hair.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

## WHAT IS CLAIMED IS:

1. A hair care composition comprising:
  - (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1 and about 420nm; and
  - 5 (b) a hair care active--selected--from the group consisting of a deterative surfactant, a conditioning agent, a fixative polymer, and mixtures thereof.
2. The hair care composition according to Claim 1 further comprising a carrier.
3. The hair care composition according to Claim 1 wherein the optical brightener has a molar extinct coefficient of at least about 50,000.
4. The hair care composition according to Claim 1 wherein the absorption peak is between a wavelength of about 200nm and about 420nm.
5. The hair care composition according to any of Claims 1 through 4 wherein the optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.
6. A hair care composition comprising:
  - (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1 and about 420nm;
  - 5 (b) a scattering particle having an average particle size of at least about 0.03  $\mu\text{m}$ ; and
  - (c) a carrier.
7. The hair care composition according to Claim 6 wherein the scattering particle is selected from the group consisting of silicones, oils, antimicrobial agents, crystalline suspending agents, metal oxides, and mixtures thereof.

8. The hair care composition according to Claim 6 wherein the optical brightener has a molar extinct coefficient of at least about 50,000.

9. The hair care composition according to Claim 6 wherein the absorption peak is between a wavelength of about 200nm and about 420nm.

10. The hair care composition according to any of Claims 6 through 9 wherein the optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.

11. The hair care composition according to Claim 10 wherein the scattering particle has an average particle size of from about 0.03 $\mu$ m to about 50 $\mu$ m.

12. The hair care composition according to Claim 11 wherein the scattering particle has an average particle size of from about 0.1 $\mu$ m to about 50 $\mu$ m.

13. The hair care composition according to Claim 10 comprising by weight from about 0.001% to about 20% of the optical brightener.

14. The hair care composition according to Claim 10 comprising by weight from about 0.01% to about 20% of the scattering particle.

15. The hair care composition according to Claim 10 further comprising a hair care active selected from the group consisting of a deterative surfactant, a conditioning agent, a fixative polymer, and mixtures thereof.

16. A method of protecting the hair from UV light by applying an optical brightener to the hair.

17. The method of protecting the hair from UV light according to Claim 16 wherein the optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.

18. A method of protecting the hair from UV light by applying to the hair a composition comprising:

- 5 (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1 and about 420nm; and
- (b) a hair care active selected from the group consisting of a detergent surfactant, a conditioning agent, a fixative polymer, and mixtures thereof.

19. A method of protecting the hair from UV light by applying to the hair a composition comprising:

- 5 (a) an effective amount of an optical brightener having a molar extinct coefficient of at least about 28,000 of an absorption peak between a wavelength of about 1 and about 420nm;
- (b) a scattering particle having an average particle size of at least about 0.03  $\mu\text{m}$ ; and
- (c) a carrier.

# INTERNATIONAL SEARCH REPORT

International Application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/13 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                               | Relevant to claim No. |
|------------|--|-----------------------|
| X          | EP 0 717 978 A (CURTIS HELENE IND INC) 26 June 1996<br>see page 4, line 24-27; claims 1,13,35;<br>examples 35,72 | 1-19                  |
| X          | US 4 126 674 A (MAUSNER JACK J) 21 November 1978<br>see page 4, line 45-58; example 2                            | 1-19                  |
| X          | WO 94 06409 A (COLGATE PALMOLIVE CO) 31 March 1994<br>see examples 1,2   | 1-10,<br>13-19        |
| X          | GB 1 328 108 A (UNILEVER LTD) 30 August 1973<br>cited in the application<br>see page 1, line 65-92; claim 6      | 1,2,6,<br>16,19       |
|            | -/--   |                       |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 June 1998

Date of mailing of the international search report

02/07/1998

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# INTERNATIONAL SEARCH REPORT

In International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| X          | GB 2 307 639 A (GEN ELECTRIC) 4 June 1997<br>cited in the application<br>see page 8, line 3 - page 9, line 14;<br>claims 1-9,11,12<br>---                                | 1-5,<br>16-18         |
| X          | US 3 658 985 A (OLSON FRANK WESLEY JR ET AL) 25 April 1972<br>cited in the application<br>see column 1, line 62 - column 2, line 27;<br>claims 1-13; examples 1-5<br>--- | 1-5,<br>16-18         |
| X          | GB 746 864 A ((COLGATE PALMOLIVE)) 21 March 1956<br>see column 1, line 11-24<br>see column 2, line 59 - column 3, line 69<br>see claims; examples 1-3<br>---             | 1-5,<br>16-18         |
| X          | US 4 312 855 A (GRAND PAUL S) 26 January 1982<br>cited in the application<br>see column 5, line 45 - column 7, line 3<br>see claims; example 11<br>* Table III *<br>---  | 1-5,<br>16-18         |
| E          | EP 0 834 303 A (KAO CORP) 8 April 1998<br><br>see examples 9,13<br>---   | 1-5,<br>16-18         |
| X          | US 3 577 528 A (EDMAN WALTER W ET AL) 4 May 1971<br>cited in the application<br>see example 7<br>---   | 1-5,<br>16-18         |
| X          | CA 1 255 603 A (COSMEPRO INC LAB) 13 June 1989<br>cited in the application<br>see page 3, line 13 - page 4, line 9;<br>claims 1-16<br>---                                | 1-5,<br>16-18         |
| X          | US 3 810 478 A (OLSON F ET AL) 14 May 1974<br><br>see column 5, line 46-52; example 2<br>---   | 1-5,<br>16-18         |
| X          | EP 0 733 355 A (KAO CORP) 25 September 1996<br>see example 2<br>---  | 1-5,<br>16-18         |
| X          | GB 1 368 316 A (OREAL) 25 September 1974<br><br>see example 7<br>---   | 1-5,<br>16-18         |
| 2 X        | US 4 676 915 A (STELTENKAMP ROBERT J ET AL) 30 June 1987<br>see example 2<br>---   | 1-5,<br>16-18         |
| 5          | ---  | ---                   |

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/16406

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.  |
|----------|---|------------------------|
| X        | EP 0 754 443 A (WELLA AG) 22 January 1997<br>see claims; examples 26-34<br>---  | 1-5,<br>16-18          |
| X        | US 3 592 581 A (SHANSKY ALBERT ET AL) 13 July 1971<br>see column 9, line 60-70<br>---   | 1-5,<br>16-18          |
| X        | US 4 938 954 A (GROSS PAUL ET AL) 3 July 1990<br>see example 5<br>---   | 1-5,<br>16-18          |
| X        | WO 97 18795 A (OREAL ;AUDOUSSET MARIE PASCALE (FR); MONDET JEAN (FR)) 29 May 1997<br>see page 13, line 9-20; example 2<br>--- | 1-6,<br>8-10,<br>13-19 |
| X        | DE 26 32 810 A (HENKEL KGAA) 26 January 1978<br>see examples<br>---   | 1-5,<br>16-18          |
| X        | DE 21 60 136 A (INT FLAVORS & FRAGRANCES INC) 20 June 1973<br>see the whole document<br>---                                   | 16,17                  |
| A        | EP 0 336 709 A (DOW CORNING) 11 October 1989<br>see claims 2,5,20-22<br>---   | 1-19                   |
| A        | GB 759 385 A (GILLETTE COMPANY) 17 October 1956<br>see page 2, line 30-70<br>-----  | 1-19                   |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/US 97/16406

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)   | Publication<br>date  |
|---|---------------------|--|--|
| EP 0717978 A                              | 26-06-1996          | US 5589177 A<br>AU 4026395 A<br>AU 688632 B<br>AU 4027195 A<br>CA 2163854 A<br>CN 1138982 A<br>FI 955866 A<br>NO 954916 A<br>NZ 280599 A<br>ZA 9510058 A                     | 31-12-1996<br>13-06-1996<br>12-03-1998<br>13-06-1996<br>07-06-1996<br>01-01-1997<br>07-06-1996<br>07-06-1996<br>27-07-1997<br>04-06-1996               |
| US 4126674 A                              | 21-11-1978          | AR 218450 A<br>AU 508026 B<br>AU 2504877 A<br>BR 7702988 A<br>CA 1091585 A<br>DE 2721278 A<br>FR 2350835 A<br>JP 1391716 C<br>JP 53004010 A<br>JP 61054767 B<br>ZA 7702805 A | 13-06-1980<br>06-03-1980<br>16-11-1978<br>20-12-1977<br>16-12-1980<br>24-11-1977<br>09-12-1977<br>23-07-1987<br>14-01-1978<br>25-11-1986<br>26-04-1978 |
| WO 9406409 A                              | 31-03-1994          | AU 4928393 A<br>CN 1089830 A<br>MX 9305746 A<br>US 5580494 A<br>ZA 9306928 A   | 12-04-1994<br>27-07-1994<br>31-05-1994<br>03-12-1996<br>20-03-1995   |
| GB 1328108 A                              | 30-08-1973          | DE 2064591 A   | 15-07-1971   |
| GB 2307639 A                              | 04-06-1997          | DE 19646804 A<br>FR 2741261 A<br>JP 9183714 A  | 22-05-1997<br>23-05-1997<br>15-07-1997   |
| US 3658985 A                              | 25-04-1972          | AT 302534 A<br>BE 753955 A<br>CH 531884 A<br>DE 2034295 A<br>DK 125620 B   | 15-09-1972<br>31-12-1970<br>31-12-1972<br>11-02-1971<br>19-03-1973   |



# INTERNATIONAL SEARCH REPORT

Information on patent family members

In .tional Application No

PCT/US 97/16406

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)   | Publication<br>date  |
|---|---------------------|--|--|
| US 3658985 A                              |                     | FR 2053194 A<br>GB 1307644 A<br>NL 7011176 A<br>SE 351564 B<br>ZA 7004430 A  | 16-04-1971<br>21-02-1973<br>01-02-1971<br>04-12-1972<br>23-02-1972   |
| GB 746864 A                               |                     | BE 522974 A<br>FR 1094336 A  | 18-05-1955   |
| US 4312855 A                              | 26-01-1982          | US 3875071 A<br>US 3832310 A<br>AR 196483 A<br>AT 322708 B<br>AU 3452671 A<br>BE 775158 A<br>CA 970909 A<br>CA 955390 A<br>DE 2155224 A<br>FR 2114751 A<br>GB 1357960 A<br>NL 7115801 A<br>SE 401608 B<br>US 3703480 A<br>US 3726815 A | 01-04-1975<br>27-08-1974<br>06-02-1974<br>10-06-1975<br>19-04-1973<br>01-03-1972<br>15-07-1975<br>01-10-1974<br>18-05-1972<br>30-06-1972<br>26-06-1974<br>18-05-1972<br>22-05-1978<br>21-11-1972<br>10-04-1973 |
| EP 0834303 A                              | 08-04-1998          | DE 19640792 C<br>DE 19640831 C   | 05-03-1998<br>05-03-1998   |
| US 3577528 A                              | 04-05-1971          | DE 1617808 A<br>GB 1152972 A<br>NL 6703673 A   | 08-04-1971<br>21-05-1969<br>28-11-1967   |
| CA 1255603 A                              | 13-06-1989          | NONE   |  |
| US 3810478 A                              | 14-05-1974          | CA 1020464 A<br>GB 1414243 A   | 08-11-1977<br>19-11-1975   |
| EP 0733355 A                              | 25-09-1996          | DE 19509981 A<br>JP 8259426 A<br>US 5635461 A  | 19-09-1996<br>08-10-1996<br>03-06-1997   |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/US 97/16406

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| GB 1368316 A                              | 25-09-1974          | AT 327395 B                | 26-01-1976          |
|   |                     | AU 471629 B                | 29-04-1976          |
|   |                     | AU 3470271 A               | 03-05-1973          |
|   |                     | BE 774082 A                | 18-04-1972          |
|   |                     | CA 968711 A                | 03-06-1975          |
|   |                     | CH 564347 A                | 31-07-1975          |
|   |                     | DE 2151789 A               | 20-04-1972          |
|   |                     | FR 2111698 A               | 09-06-1972          |
|   |                     | LU 61889 A                 | 28-06-1972          |
|   |                     | NL 7114310 A               | 21-04-1972          |
|   |                     | US 3989447 A               | 02-11-1976          |
| US 4676915 A                              | 30-06-1987          | IN 172493 A                | 04-09-1993          |
|   |                     | US 4682982 A               | 28-07-1987          |
|   |                     | US 4619775 A               | 28-10-1986          |
|   |                     | AT 395161 B                | 12-10-1992          |
|   |                     | AU 5847686 A               | 24-12-1986          |
|   |                     | BE 904932 A                | 16-12-1986          |
|   |                     | BR 8602787 A               | 10-02-1987          |
|   |                     | DE 3619807 A               | 18-12-1986          |
|   |                     | DK 283386 A                | 18-12-1986          |
|   |                     | EG 17896 A                 | 30-10-1992          |
|   |                     | FI 862521 A, B             | 18-12-1986          |
|   |                     | FR 2583425 A               | 19-12-1986          |
|   |                     | GB 2176814 A, B            | 07-01-1987          |
|   |                     | IN 171622 A                | 28-11-1992          |
|   |                     | IN 171860 A                | 23-01-1993          |
|   |                     | JP 61291675 A              | 22-12-1986          |
|   |                     | KR 9405274 B               | 15-06-1994          |
|   |                     | LU 86475 A                 | 13-01-1987          |
|   |                     | NL 8601562 A               | 16-01-1987          |
|   |                     | PT 82755 B                 | 13-10-1987          |
|   |                     | SE 8602608 A               | 18-12-1986          |
|   |                     | AT 127186 A, B             | 15-07-1993          |
|   |                     | AU 594337 B                | 08-03-1990          |
|   |                     | AU 5723286 A               | 20-11-1986          |
|   |                     | AU 616387 B                | 31-10-1991          |
|   |                     | AU 8192287 A               | 09-06-1988          |
|   |                     | BE 904782 A                | 17-11-1986          |
|   |                     | BE 1000498 A               | 27-12-1988          |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In: International Application No

PCT/US 97/16406

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| US 4676915 A                              |                     | CA 1335206 A               | 11-04-1995          |
|   |                     | CA 1284254 A               | 21-05-1991          |
|   |                     | CH 677856 A, B             | 15-07-1991          |
|   |                     | CH 675439 A                | 28-09-1990          |
|   |                     | DE 3615500 A               | 20-11-1986          |
|   |                     | DE 3740193 A               | 16-06-1988          |
|   |                     | FR 2581992 A               | 21-11-1986          |
|   |                     | FR 2609040 A               | 01-07-1988          |
|   |                     | GB 2178028 A, B            | 04-02-1987          |
|   |                     | GB 2198462 A, B            | 15-06-1988          |
|   |                     | IE 59149 B                 | 12-01-1994          |
|   |                     | JP 61293285 A              | 24-12-1986          |
|   |                     | JP 63170496 A              | 14-07-1988          |
|   |                     | LU 86428 A                 | 05-12-1986          |
|   |                     | LU 87060 A                 | 14-07-1988          |
|   |                     | NL 8601258 A               | 16-12-1986          |
|   |                     | NL 8702953 A               | 01-07-1988          |
|   |                     | SE 8602188 A               | 17-11-1986          |
|   |                     | SE 8704852 A               | 09-06-1988          |
|   |                     | US 4764291 A               | 16-08-1988          |
|   |                     | US 4714559 A               | 22-12-1987          |
|   |                     | US 4715970 A               | 29-12-1987          |
| EP 0754443 A                              | 22-01-1997          | DE 19525821 A              | 16-01-1997          |
|   |                     | ES 2098208 T               | 01-05-1997          |
|   |                     | JP 9030937 A               | 04-02-1997          |
| US 3592581 A                              | 13-07-1971          | NONE                       |                     |
| US 4938954 A                              | 03-07-1990          | DE 3725080 A               | 09-02-1989          |
|   |                     | DE 3864936 A               | 24-10-1991          |
|   |                     | WO 8900845 A               | 09-02-1989          |
|   |                     | EP 0301197 A               | 01-02-1989          |
|   |                     | JP 2515149 B               | 10-07-1996          |
|   |                     | JP 2500105 T               | 18-01-1990          |
| WO 9718795 A                              | 29-05-1997          | FR 2741530 A               | 30-05-1997          |
|   |                     | CA 2211797 A               | 29-05-1997          |
|   |                     | EP 0808150 A               | 26-11-1997          |
|   |                     | JP 10502945 T              | 17-03-1998          |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/16406

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)   | Publication<br>date  |
|---|---------------------|--|--|
| DE 2632810 A                              | 26-01-1978          | NONE   |  |
| DE 2160136 A                              | 20-06-1973          | US 3712947 A<br>US 3625976 A   | 23-01-1973<br>07-12-1971   |
| EP 0336709 A                              | 11-10-1989          | US 4866152 A<br>CA 1337524 A<br>JP 2011662 A<br>JP 2542077 B<br>US 4982603 A<br>US 4962177 A | 12-09-1989<br>07-11-1995<br>16-01-1990<br>09-10-1996<br>08-01-1991<br>09-10-1990 |
| GB 759385 A                               |                     | NONE   |  |